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Plutonium Isotopic Composition by Gamma-Ray Spectroscopy: A Review

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PLUTONIUM ISOTOPIC COMPOSITION BY GAMMA-RAY SPECTROSCOPY: A REVIEW

by

T. E. Sampson

ABSTRACT

This report presents a review of the methods and capabilities of nondestructive measurements of the isotopic composition of plutonium using gamma-ray spectroscopy.

I. INTRODUCTION

Accurate and timely accounting for and control of plutonium require that methods be available for measuring plutonium in its various forms. Measurements of the amount of individual isotopes as well as the total amount of plutonium are often required. Gamma-ray spectroscopy techniques can measure the absolute amounts of the various plutonium isotopes in many kinds of samples. The idea of expanding these measurements to all isotopes to determine the isotopic distribution of the plutonium has appealed to gamma-ray spectroscopists for many years.

Starting in the early 1970s, researchers developed several approaches, some of which are described in Refs. 1-5. The characteristics of the many kinds of samples found in plutonium processing plants make it impossible to find one method that is optimum for all sample types. Instead, the history of these nondestructive isotopic measurements shows that the method was often tailored to the specific sample type. Different methods have been developed for solutions vs solids, freshly separated samples (americium and uranium removed) vs aged ones, and low-burnup material vs high-burnup material.

Before we discuss the principles of isotopic measurements, we will introduce some of the characteristics of plutonium spectra that influence the approach to isotopic measurements. We will describe useful spectral regions and then present the principles of spectral analysis for isotopic analysis.

Typical data collection hardware and caveats will be described, followed by details of data analysis methods. A description of several implemented systems then follows with examples of their accuracy and precision.

II. PRELIMINARY CONSIDERATIONS

A. Plutonium Isotope Decay Characteristics

Most plutonium samples contain the isotopes ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu. Americium-241, a decay product of ^{241}Pu, is always present, as is ^{237}U, another decay product. When considering the total heat output of a sample measured by calorimetry, ^{241}Am becomes important because of its relatively short half-life and high specific power. Table I lists some of the decay characteristics of these important isotopes.

TABLE I

DECAY CHARACTERISTICS FOR ISOTOPES USEFUL IN PLUTONIUM ISOTOPIC MEASUREMENTS

Isotope	Half-Life (yr)	Activity (dis/s•g)	Specific Power (mW/g Isotope)
^{238}Pu	87.74 ± 0.04	6.3330×10^{11}	567.57 ± 0.26
^{239}Pu	24119 ± 26	2.2942×10^{9}	1.9288 ± 0.0003
^{240}Pu	6564 ± 11	8.3945×10^{9}	7.0824 ± 0.0020
^{241}Pu	14.348 ± 0.022	3.8244×10^{12}	3.412 ± 0.002
^{242}Pu	376300 ± 900	1.4522×10^{8}	0.1159 ± 0.0003
^{241}Am	433.6 ± 1.4	1.2655×10^{11}	114.20 ± 0.42
^{237}U	6.75 days	9.4080×10^{7}[a]	-

[a] Plutonium-241-^{237}U equilibrium assumed (see Fig. 1). Alpha branching ratio of ^{241}Pu assumed to be 2.46×10^{-5}.

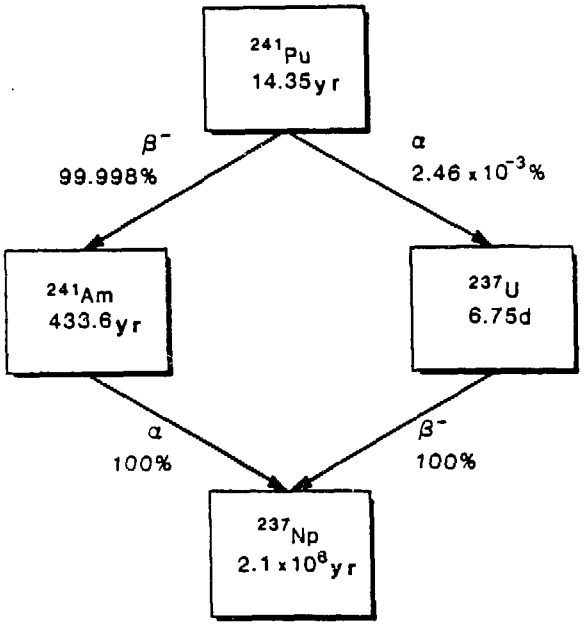

Fig. 1. Decay modes of ^{241}Pu.

B. ^{241}Pu Decay

The decay characteristics of ^{241}Pu shown in Fig. 1 become important for plutonium isotopic measurements. The long half-life of its ^{241}Am daughter (relative to ^{241}Pu) means that ^{241}Am concentration continues to increase for decay times up to 75 years. Old plutonium samples often have very high ^{241}Am content, especially if a large amount of ^{241}Pu was initially present.

The short half-life of the ^{237}U daughter means that it rapidly comes into secular equilibrium[6] with its ^{241}Pu parent. After about seven half-lives have elapsed, the decay rate of ^{237}U becomes the same as the decay rate of ^{241}Pu. After that time, gamma rays from the decay of ^{237}U can be used as a measure of the amount of ^{241}Pu in a sample. Because ^{237}U has several strong gamma rays, it becomes an important isotope for plutonium isotopic measurements. We will refer to samples where ^{237}U is in secular equilibrium with ^{241}Pu as "^{241}Pu-^{237}U equilibrium" or "aged" samples. About 99% of equilibrium is attained in 45 days after complete removal or separation of ^{237}U from a sample. We call samples where ^{241}Pu-^{237}U equilibrium does not exist "freshly separated." For those samples, ^{237}U cannot be used as a measure of ^{241}Pu.

We also observe in Fig. 1 that both ^{241}Am and ^{237}U decay to the same isotope, ^{237}Np. Many of these decays populate the same excited states in ^{237}Np and give rise to identical gamma rays. Thus, most of the useful ^{237}U gamma rays have a contribution from the ^{241}Am in the sample. The amount of this interference depends upon the particular gamma ray and how long the ^{241}Am has grown into the sample. Figure 2 shows the relative contributions for important ^{237}U gamma rays where it has been assumed that all ^{237}U and ^{241}Am were removed from the sample at t = 0. A correction should be made to ^{241}Pu-^{237}U peaks for their ^{241}Am content.

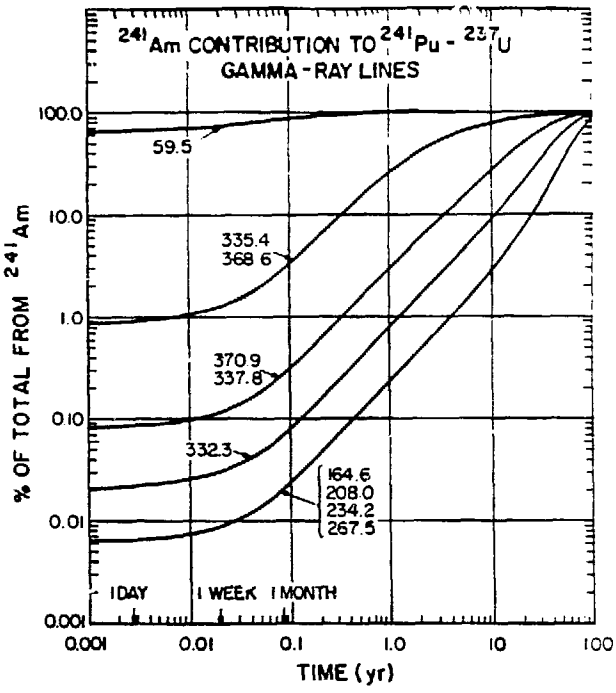

Fig. 2. Americium-241 contribution to gamma rays from the decay of ^{237}U. Legend is gamma-ray energies in keV. All uranium and americium assumed to be removed at t = 0.

C. ^{242}Pu

Plutonium-242 has only a few gamma rays, similar in energy and branching ratio to those from ^{240}Pu. However, its long half-life and low abundance make its detection by gamma-ray measurement impossible. Instead, experimenters resort to the use of empirical isotopic correlations[7] to predict the ^{242}Pu content, given knowledge of the other isotopic fractions. This generally produces acceptable results for the small concentrations of ^{242}Pu (typically 0.03% to 5%) found in most plutonium.

D. Spectral Interferences

Many regions of the spectrum of gamma rays can contain interferences from gamma rays from other isotopes in the sample. Very-high-burnup samples will often have ^{243}Am and its ^{239}Np daughter. Aged samples may have the ^{233}Pu daughter of ^{237}Np. Fission products can be present in some cases. One cannot list all the possible interferences here, but it suffices to say that the spectroscopist should try to know the sample history in order to anticipate possible spectral interferences.

E. Applications

The principal application of plutonium isotopic measurements is to support other nondestructive assay (NDA) methods to provide measurements of the total plutonium content of the sample. Calorimetry and neutron coincidence counting can utilize plutonium isotopic results.

Calorimetry uses the isotopic information to calculate the specific power of the sample, P(W/g Pu), from the measured isotopic fractions f_i and the known specific power for each isotope K_i (W/g isotope). From the variables, the sample specific power is given by

$$P = \sum_i f_i K_i \ ,$$

where

$$i = {}^{238}Pu,\ {}^{239}Pu,\ {}^{240}Pu,\ {}^{241}Pu,\ {}^{242}Pu, \text{ and } {}^{241}Am.$$

For neutron coincidence counting only the even isotopes--^{238}Pu, ^{240}Pu, and ^{242}Pu--are important, with the measurement giving a value for the effective g ^{240}Pu in the sample. The known isotopic composition is used to convert the effective g ^{240}Pu into total plutonium using the expression

$$f_{240}(\text{eff}) = 2.49\ f_{238} + f_{240} + 1.57\ f_{242} \ .$$

The f's denote the isotopic fraction of the subscripted isotope.

III. SPECTRAL REGIONS USEFUL FOR ISOTOPIC MEASUREMENTS

To fully understand the different methods developed for isotopic measurement of plutonium by gamma-ray spectroscopy, one must be familiar with the spectral features in the various regions of the gamma-ray spectrum from all types of samples. The energies and branching ratios used in the following tables come from the widely used work of Gunnink et al.[8] The spectral regions discussed below follow those suggested in Ref. 8 and further discussed in the guide published by Lemming and Rakel.[9] Different burnup, hence different isotopic distributions, and, especially, different ^{241}Am concentrations can greatly affect the number and intensity of gamma rays appearing in the spectrum. Figures 3 and 4 show two examples, with Fig. 3 representing low

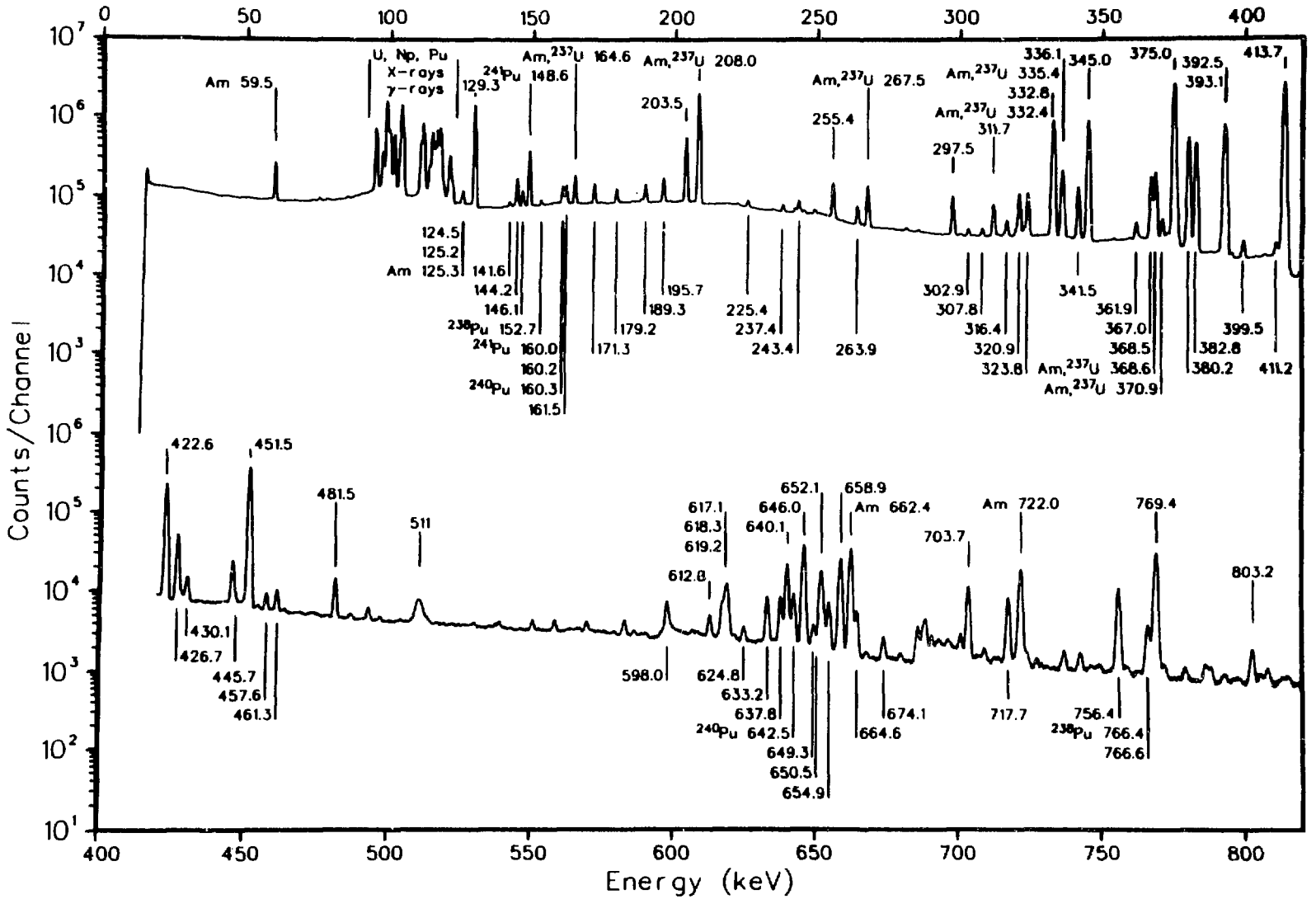

Fig. 3. Spectrum from 500 g of plutonium metal with isotopic composition (wt%): 238, 0.012%; 239, 93.82%; 240, 5.90%; 241, 0.240%; 242, 0.02%; and ^{241}Am, 630 μg/g Pu. Detector is an 11.7% relative efficiency coax with 1.75-keV resolution at 1332 keV. Energies not labeled with a specific isotope are from ^{239}Pu.

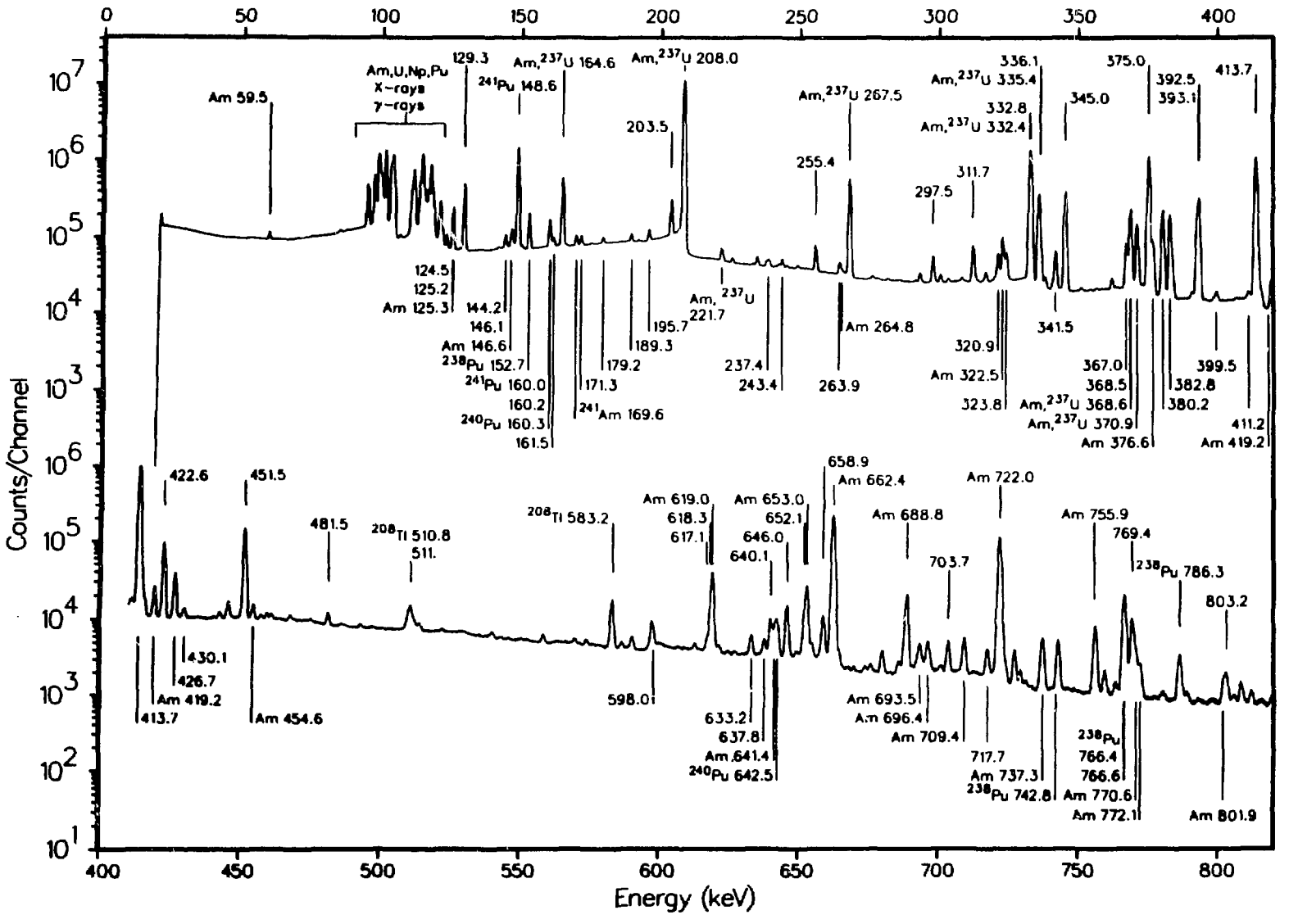

Fig. 4. Spectrum from 530 g plutonium as PuO_2 with isotopic composition (wt%): 238, 0.202%; 239, 82.49%; 240, 13.75%; 241, 2.69%; 242, 0.76%; Am, 11 800 μg/g Pu. Detector is a 10.2% relative efficiency coax with 1.65-keV resolution at 1332 keV. Energies not labeled with a specific isotope are from ^{239}Pu.

burnup and low ^{241}Am and Fig. 4 representing intermediate burnup and relatively high ^{241}Am. The discussion and figures for each spectral region attempt to illustrate reasonable extremes.

Table II lists most of the useful gamma rays for plutonium isotopic measurements with their activity in gamma rays per second per gram of isotope. We observe that the lower-energy gamma rays are more intense than those at higher energies. It is desirable to use these whenever possible, but experimental and sample considerations often make this impossible.

A. 40-keV Region

This region has been used mainly for the analysis of freshly separated solutions from which ^{241}Am and ^{237}U have been removed. If too much ^{241}Am is present, its 60-keV gamma ray will overwhelm all other peaks in the region, making this region useless for isotopic measurements. Usually, this region can be used for times up to about 15 to 30 days after a separation of americium and uranium. Figure 5 shows a typical spectrum from a high-burnup reprocessing plant solution[10] and Table III lists peak energies and intensities. If it is accessible, this is the most useful region for ^{238}Pu, ^{239}Pu, and ^{240}Pu. Measurement of ^{241}Pu is usually obtained from its 148.6-keV gamma ray. Small contributions from ^{241}Pu and ^{237}U interfere with the main ^{238}Pu peak at 43.5 keV, the ^{240}Pu peak at 45.2 keV, and the ^{239}Pu peak at 51.6 keV.

Several experimenters have used this region for solution measurements. Gunnink et al.[11] and Russo et al.[10] have measured freshly separated reprocessing plant solutions; Umezawa et al.[12] and Bubernak[13] have applied these measurements to samples prepared in an analytical laboratory. Li et al.[14] have also used this region for submilligram-sized solid samples with modest ^{241}Am content.

We have not yet discussed data analysis techniques, but we will mention them in general reference to the different methods used to analyze data in the 40-keV region. The next subsection will describe the analysis methods in more detail.

Gunnink[11] uses absolute counting techniques employing calibration with known solution standards. Umezawa et al.[12] also use absolute counting with a calibrated detector, whereas Bubernak[13] calibrates with samples of known isotopic composition. Russo et al.[10] and Li et al.[14] measure isotopic

TABLE II

USEFUL GAMMA RAYS IN VARIOUS ENERGY REGIONS

Region (keV)	^{238}Pu (keV)	^{238}Pu (γ/s•g)	^{239}Pu (keV)	^{239}Pu (γ/s•g)	^{240}Pu (keV)	^{240}Pu (γ/s•g)	^{241}Pu (keV)	^{241}Pu (γ/s•g)	^{241}Am (keV)	^{241}Am (γ/s•g)
40-60	43.48	2.49×10^{8}	51.63	6.19×10^{5}	45.23	3.80×10^{6}	-		59.54	4.54×10^{10}
90-105[a]	99.86	4.59×10^{7}	98.78	2.80×10^{4}	104.24	5.86×10^{5}	103.68	3.86×10^{6}	98.95	2.57×10^{7}
									102.97	2.47×10^{7}
120-450	152.68	6.05×10^{6}	129.29	1.44×10^{5}	160.28	3.38×10^{4}	148.57	7.15×10^{6}	125.29	5.16×10^{6}
			203.54	1.28×10^{4}			164.58	1.73×10^{6} [b]	335.40	6.28×10^{5}
			345.01	1.28×10^{4}			208.00	2.04×10^{7} [b]		
			375.04	3.60×10^{4}			332.35	1.14×10^{6} [b]		
			413.71	3.42×10^{4}			370.93	1.04×10^{5} [b]		
450-800	766.41	1.39×10^{5}	645.97	3.42×10^{2}	642.48	1.05×10^{3}	-		662.42	4.61×10^{5}
			717.72	6.29×10^{1}					721.99	2.18×10^{5}

[a]There are also intense x rays in this region arising from all the isotopes. Although they are not listed here, they may be used for isotopic measurements under certain conditions. See Table IV for intensities.

[b]Uranium-237 daughter of ^{241}Pu with ^{241}Pu-^{237}U equilibrium.

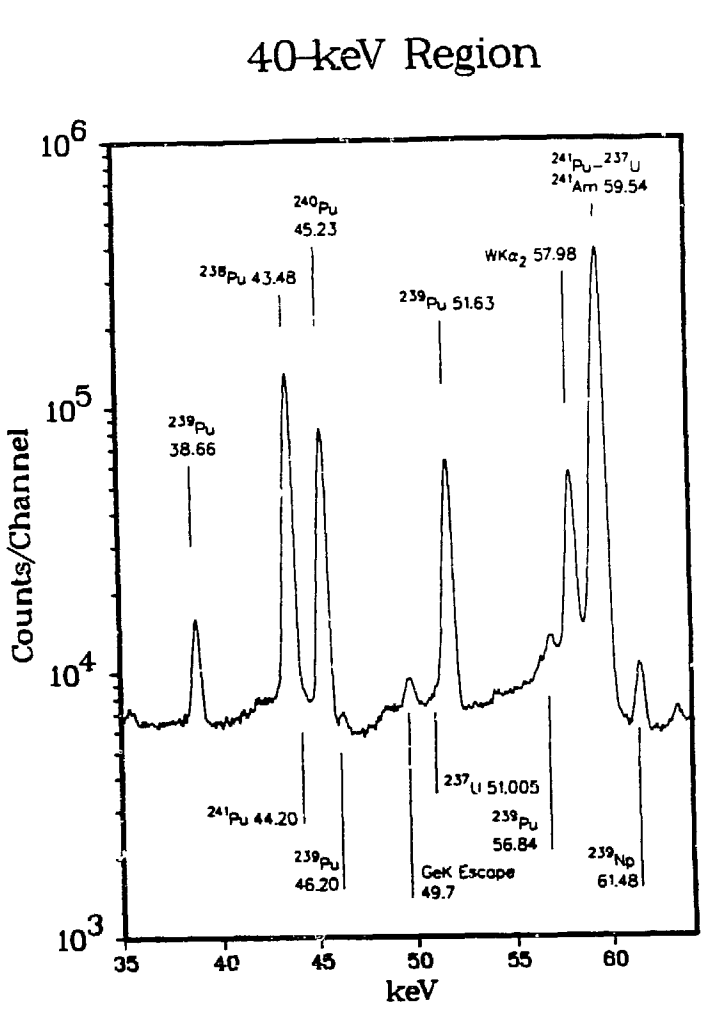

Fig. 5. Freshly separated 185-g/ℓ solution of plutonium in nitric acid. Isotopic composition (wt%): 238, 0.649%; 239, 67.01%; 240, 21.80%; 241, 8.11%; 242, 2.44%. The WKα_2 x ray arises from shielding around the detector (Ref. 10).

ratios, making the measurements independent of calibration standards. This is necessary for the measurements of Li et al.[14] because the samples do not have reproducible geometry.

B. 100-keV Region

This region is the most complex of all regions of the gamma-ray spectrum of plutonium. Table IV tabulates 14 gamma rays and x rays. The uranium x rays arise from plutonium decay and can be used to measure the amount of some plutonium isotopes. Neptunium x rays arise from the decay of ^{241}Am and ^{237}U,

TABLE III

PEAK ENERGIES AND INTENSITIES IN 40-keV REGION[8]

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s•g)
^{239}Pu	38.664	1.050 E - 04	1.00	2.4089 E + 05
	40.410	1.620 E - 06	10.00	3.7165 E + 03
	42.060	1.650 E - 06	3.00	3.7854 E + 03
$^{237}U^{a}$	43.430	5.904 E - 09	7.00	2.2579 E + 04
^{238}Pu	43.477	3.930 E - 04	0.30	2.4889 E + 08
^{241}Pu	44.200	4.180 E - 08		1.5986 E + 05
	44.860	8.360 E - 09		3.1972 E + 04
^{240}Pu	45.232	4.530 E - 04	0.20	3.8039 E + 06
^{239}Pu	46.210	7.370 E - 06	10.00	1.6908 E + 04
	46.690	5.800 E - 07	6.00	1.3306 E + 03
$^{237}U^{a}$	51.005	8.364 E - 08	2.00	3.1987 E + 05
^{239}Pu	51.629	2.700 E - 04	0.20	6.1942 E + 05
	54.040	2.000 E - 06	1.40	4.5883 E + 03
^{241}Pu	56.320	2.500 E - 08		9.5610 E + 04
^{239}Pu	56.760	9.750 E - 09		3.7288 E + 04
	56.838	1.130 E - 05	1.00	2.5924 E + 04
$^{237}U^{a}$	59.536	8.487 E - 06	0.20	3.2458 E + 07
^{241}Am	59.536	3.590 E - 01		4.5432 E + 10
$^{237}U^{a}$	64.832	3.198 E - 07	0.50	1.2230 E + 06

[a] Uranium-237 activity computed assuming ^{241}Pu-^{237}U equilibrium. Uranium-237 branching ratio includes 2.46×10^{-5} ^{241}Pu alpha branch to ^{237}U.

TABLE IV

PEAK ENERGIES AND INTENSITIES IN 100-keV REGION[8]

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s•g)	X Ray
^{238}Pu	94.658	1.050 E - 06	1.40	6.6497 E + 05	UKα2
^{239}Pu	94.658	4.220 E - 05	0.25	9.6813 E + 04	UKα2
^{240}Pu	94.658	6.360 E - 07	5.00	5.3406 E + 03	UKα2
^{241}Pu	94.658	3.030 E - 06	0.50	1.1588 E + 07	UKα2
^{239}Pu	96.130	2.230 E - 07	20.00	5.1160 E + 02	
^{237}U[a]	97.071	3.887 E - 06	0.40	1.4865 E + 07	NpKα2
^{241}Am	97.072	1.180 E - 05	2.00	1.4933 E + 06	NpKα2
^{238}Pu	98.441	1.690 E - 06	1.00	1.0703 E + 06	UKα1
^{239}Pu	98.441	6.760 E - 05	0.30	1.5508 E + 05	UKα1
^{240}Pu	98.441	1.020 E - 06	5.00	8.5651 E + 03	UKα1
^{241}Pu	98.441	4.850 E - 06	0.50	1.8548 E + 07	UKα1
^{239}Pu	98.780	1.220 E - 05	3.00	2.7989 E + 04	
^{241}Am	98.951	2.030 E - 04	0.50	2.5690 E + 07	
Pu	99.530				PuKα2
^{238}Pu	99.864	7.240 E - 05	0.20	4.5851 E + 07	
^{237}U[a]	101.066	6.199 E - 06	0.30	2.3708 E + 07	NpKα1
^{241}Am	101.066	1.900 E - 05	1.40	2.4045 E + 06	NpKα1
^{241}Am	102.966	1.950 E - 04	0.50	2.4677 E + 07	
^{239}Pu	103.020	2.170 E - 06	1.60	4.9783 E + 03	
^{241}Pu	103.680	1.010 E - 06	0.50	3.8627 E + 06	
Pu	103.748				PuKα1
^{240}Pu	104.244	6.980 E - 05	0.40	5.8612 E + 05	

[a]Uranium-237 activity computed assuming ^{241}Pu-^{237}U equilibrium. Uranium-237 branching ratio includes 2.46×10^{-5} ^{241}Pu alpha branch to ^{237}U.

whereas the plutonium x rays appear in larger or more concentrated samples from gamma-ray and alpha-particle-induced x-ray fluorescence. Gamma rays are present from all the principal plutonium isotopes. This is the only region where these conditions exist. Branching intensities are generally larger than those at higher energies (^{239}Pu is an exception) and smaller than those in the 40-keV region (^{241}Pu is the exception).

Figure 6 shows the strong, overlapping, interfering nature of the spectrum in this region. For low-burnup solutions, represented at the bottom of Fig. 6, the entire isotopic distribution may be determined.[4] The complexity of the region requires peak-fitting or response-function[4,15] analysis. The special case of low-burnup PuO_2 has also been treated by response-function methods. High-burnup solutions have also been analyzed using response-function methods in this region,[11] but in general, this is more difficult. The increased activity of high-burnup and high-concentration solutions gives rise to a plutonium fluorescent x ray at 103.75 keV that lies very close to the 104.24-keV ^{240}Pu gamma ray, as well as to a plutonium x ray at 99.53 keV that interferes with the 99.86-keV ^{238}Pu gamma. The different intrinsic line shape of x rays as opposed to gamma rays also must be considered in the analysis of this region by response-function methods. We will discuss this later.

C. 125-keV Region

This region is used primarily for measurement of ^{241}Am and ^{239}Pu with gamma rays at 125.29 and 129.29 keV respectively. Plutonium-239 lines at 125.21 and 124.51 keV strongly interfere with the 125.29-keV ^{241}Am gamma line. It is difficult to obtain the ^{241}Am peak area for ^{241}Am concentrations below a few hundred μg/g Pu. At an americium concentration of 500 μg/g Pu, the ^{239}Pu interferences contribute over 50% of the peak area between 124.5 and 125.3 keV. For an americium concentration of 5000 μg/g Pu, over 90% of the intensity in this region is from ^{241}Am. The ^{239}Pu interferences can be removed by peak fitting[16] or stripping.[17] Many measurements use absorbers or filters (see Sec. V.C) to reduce the count rate of lower-energy gamma rays in the spectrum. These absorbers also affect the count rate in the 125-keV region. A useful filter thickness of 0.15 cm (0.06 in.) of cadmium has a transmission of 35% at 123.5 keV, giving a factor of 3 reduction in the 125-keV count rate.

100-keV Region

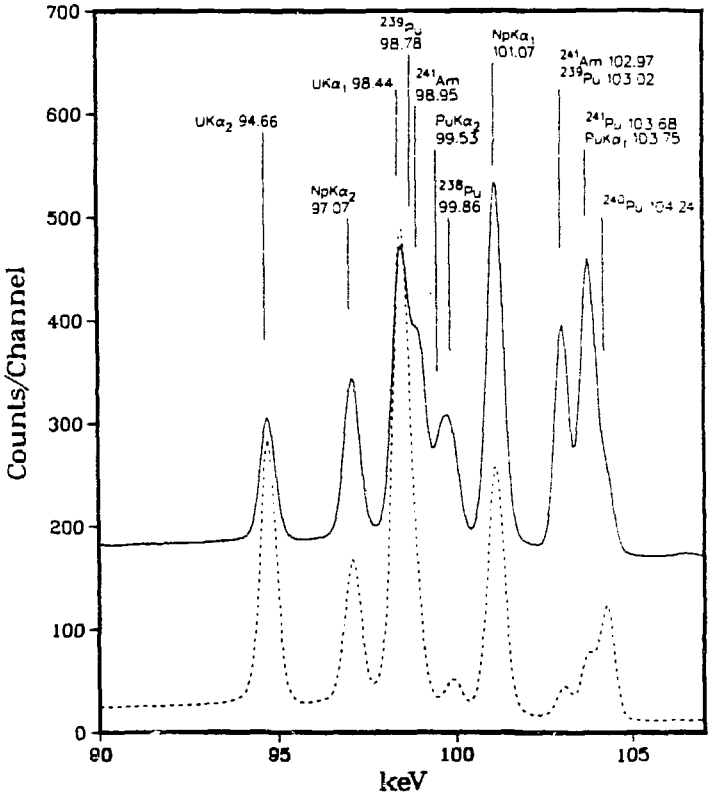

Fig. 6. Top (solid line)--530 g plutonium as PuO_2 counted with a 200-mm^2 x 10-mm-deep planar HpGe detector with resolution of 490 eV at 122 keV. Isotopic composition (wt%): 238, 0.302%; 239, 82.49%; 240, 13.75%; 241, 2.69%; 242, 0.76%; ^{241}Am, 11 800 µg/g Pu. The units of the linear counts scale are arbitrary.

Bottom (dashed line)--10 mℓ of 20 g Pu/ℓ solution in 1 M HNO_3 counted with same detector as above. Isotopic composition (wt%): 238, 0.027%; 239, 91.65%; 240, 7.68%; 241, 0.532%; 242, 0.12%; ^{241}Am, 315 µg/g Pu.

The ^{241}Am gamma ray at 125.29 keV is about 10 times weaker than the ^{241}Am gamma rays in the 100-keV region.

In the Table V listing of peak energies and intensities in this region, plutonium fluorescent Kß x rays in the 120- to 121-keV range are omitted. In the plots of Fig. 7, we see that these further complicate analysis in this region by making it difficult to find a place to establish backgrounds below

TABLE V

PEAK ENERGIES AND INTENSITIES IN 125-keV REGION[8]

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s•g)
^{239}Pu	119.708	3.000 E - 07	2.00	6.8825 E + 02
^{241}Pu	121.200	6.850 E - 09		2.6197 E + 04
^{241}Am	122.994	1.000 E - 05	0.80	1.2655 E + 06
^{239}Pu	123.620	1.970 E - 07	6.00	4.5195 E + 02
	124.510	6.130 E - 07	3.00	1.4063 E + 03
	125.210	7.110 E - 07	2.00	1.6311 E + 03
^{241}Am	125.292	4.080 E - 05	0.50	5.1633 E + 06
^{239}Pu	129.294	6.260 E - 05	0.20	1.4361 E + 05

124.5 keV. Higher-burnup material (top of Fig. 7) generally has a stronger ^{241}Am peak but a weaker ^{239}Pu peak than does low-burnup material. For high-burnup samples, not only is the ^{239}Pu peak at 129.29 keV weaker because of less ^{239}Pu in the sample, but the background continuum under the peak is usually higher because of stronger ^{241}Pu and ^{237}U gamma rays at higher energies.

D. 148-keV Region

The two most important peaks in this region are the 148.56-keV ^{241}Pu peak and the 152.68-keV ^{238}Pu peak. The 148.56-keV peak is the only useful gamma ray directly from ^{241}Pu outside of the complex 100-keV range. Likewise the 152.68-keV ^{238}Pu peak, although weak, is still the most widely used gamma ray from this isotope above 100 keV. Measurements can also use the 144.21- and 143.35-keV ^{239}Pu lines, which have an interference from the 143.76-keV ^{235}U line from samples containing ^{235}U. Americium-241 peaks at 146.56 and 150.11 keV complicate window settings and background determination for methods that use simple region-of-interest (ROI) summation for peak areas. An additional interference can arise in systems that use a ^{109}Cd reference source for absolute measurement purposes.[10,11] Here, the 88.04-keV ^{109}Cd gamma ray will sum with the 59.54-keV ^{241}Am gamma ray to produce a pileup peak at 147.6 keV. Other interferences from summing can affect the 152.68-keV ^{238}Pu peak. ($UK\alpha_2$ at 94.66 keV plus ^{241}Am at 59.54 keV equals 154.2 keV.)

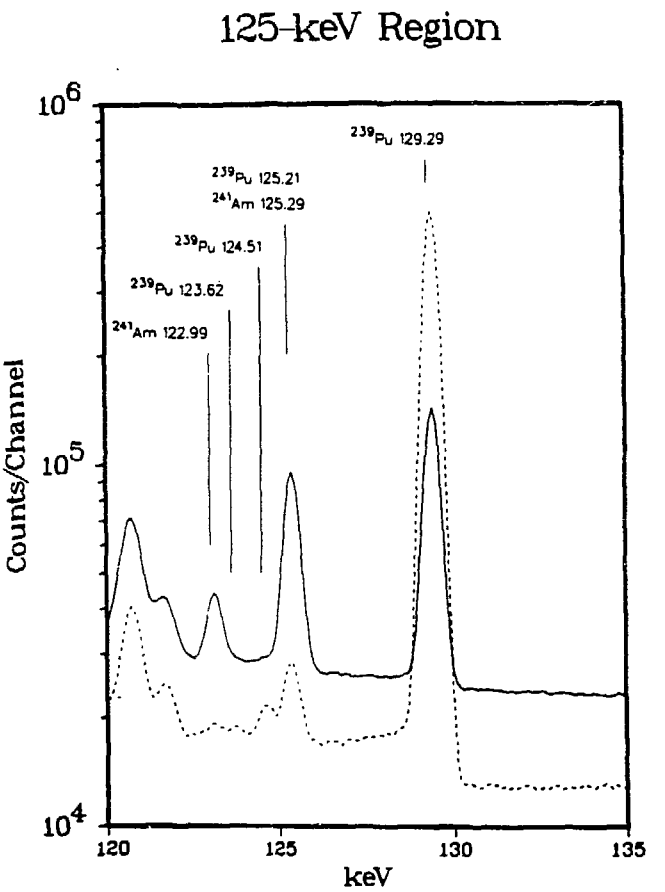

Fig. 7. Top (solid line)--PuO_2 counted with a 200-mm^2 by 10-mm-deep planar HpGe detector with resolution of 490 eV at 122 keV. Isotopic composition (wt%): 238, 0.378%; 239, 78.89%; 240, 18.28%; 241, 4.42%; 242, 1.04%; ^{241}Am, 14 300 µg/g Pu.

Bottom (dashed line)--same as top with isotopic composition (wt%): 238, 0.016%; 239, 93.51%; 240, 6.15%; 241, 0.278%; 242, 0.039%; ^{241}Am, 480 µg/g Pu.

The weak 153-keV ^{238}Pu peak on a high background continuum generally yields poor precision for low-burnup (0.01 wt% ^{238}Pu) material. This precision can be as poor as 10%, one relative standard deviation (RSD), for typical measurements. Also, for this peak, a branching ratio bias of about 2.5% is widely recognized. The accepted branching ratio is about 2.5% lower than the values in Table VI. Reference 18 discusses branching ratio biases in other energy regions. Figure 8 gives a plot of the peaks in this region from high- and low-burnup material.

TABLE VI

PEAK ENERGIES AND INTENSITIES IN 148-keV REGION[8]

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s·g)
^{239}Pu	141.657	3.200 E - 07	2.00	7.3413 E + 02
	143.350	1.730 E - 07	4.00	3.9689 E + 02
	144.211	2.830 E - 06	0.60	6.4925 E + 03
	146.077	1.190 E - 06	0.60	2.7300 E + 03
^{241}Am	146.557	4.610 E - 06	1.00	5.8340 E + 05
^{241}Pu	148.567	1.870 E - 06	0.30	7.1516 E + 06
^{241}Am	150.110	7.400 E - 07	2.00	9.3648 E + 04
^{238}Pu	152.680	9.560 E - 06	0.50	6.0544 E + 06

E. 160-keV Region

For a single-detector system not using the 100- or 40-keV regions, the 160-keV region is generally the only choice for measuring ^{240}Pu. The ^{240}Pu gamma ray at 160.28 keV has strong interferences from ^{241}Pu at 159.95 keV and ^{239}Pu at 160.19 keV. This three-peak complex (Fig. 9) is only partially resolved from the 161.45-keV ^{239}Pu line. Peak-fitting, peak-stripping, or response-function methods must be used to isolate the ^{240}Pu intensity. Even so, its statistical precision is seldom better than ~2% RSD.

Also, as burnup increases, the fraction of the 160-keV complex contributed by ^{240}Pu decreases even though the entire complex increases in intensity. Using the branching ratio data of Table VII, we illustrate in Table VIII how the relative fraction of ^{240}Pu in the 160-keV complex decreases from almost 70% for 6% ^{240}Pu to about 25% for material with 20% ^{240}Pu. This occurs because the ^{241}Pu interference increases more rapidly than ^{240}Pu as burnup increases.

The 164.58-keV peak arises from the ^{237}U daughter of ^{241}Pu; thus we can use it for ^{241}Pu measurements only after equilibrium has been attained. It must also have a correction for its ^{241}Am contribution. Summing of

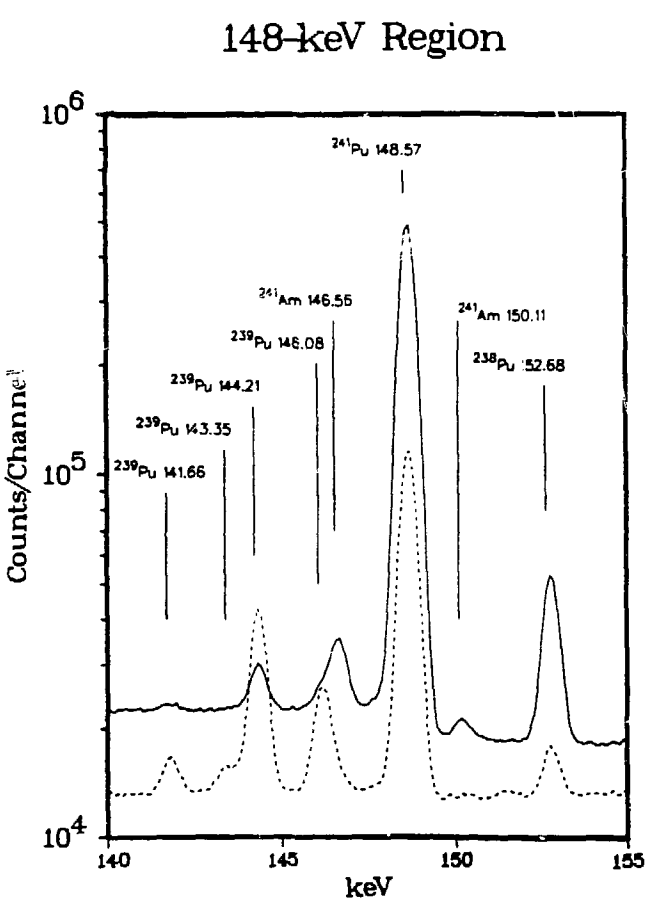

Fig. 8. Top (solid line)--PuO_2 counted with a 200-mm^2 by 10-mm-deep planar HpGe detector with resolution of 490 eV at 122 keV. Isotopic composition (wt%): 238, 0.378%; 239, 78.89%; 240, 15.28%; 241, 4.42%; 242, 1.04%; ^{241}Am, 14 300 µg/g Pu.

Bottom (dashed line)--same as top with isotopic composition (wt%): 238, 0.016%; 239, 93.51%; 240, 6.15%; 241, 0.28%; 242, 0.039%; ^{241}Am, 480 µg/g Pu.

x rays and gamma rays in the 100-keV region with the 59.5-keV ^{241}Am line can produce interferences under the 160-keV complex. The proper choice of filters can eliminate this interference.[19] The ^{235}U gamma ray at 163.35 keV can interfere with the ^{241}Pu-^{237}U line at 164.58 keV for samples with appreciable ^{235}U content (^{235}U/^{241}Pu > 1.5).

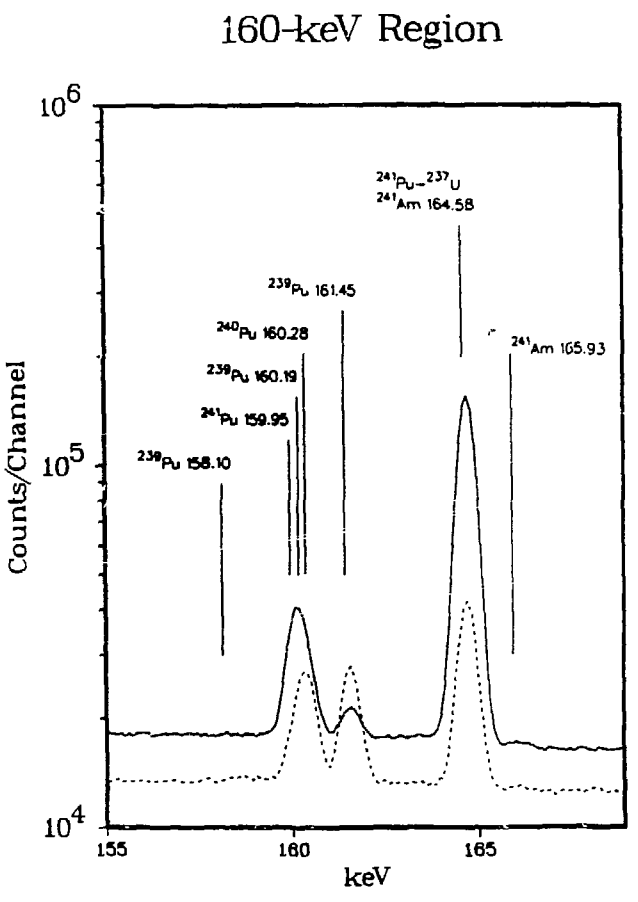

Fig. 9. Top (solid line)--PuO_2 counted with a 200-mm^2 by 10-mm-deep planar HpGe detector with resolution of 490 eV at 122 keV. Isotopic composition (wt%): 238, 0.378%; 239, 78.89%; 240, 15.28%; 241, 4.42%; 242, 1.04%; ^{241}Am, 14 300 µg/g Pu.

Bottom (dashed line)--same as top with isotopic composition (wt%): 238, 0.016%; 239, 93.51%; 240, 6.15%; 241, 0.28%; 242, 0.039%; ^{241}Am, 480 µg/g Pu.

F. 208-keV Region

The strong ^{241}Pu-^{237}U line at 208.00 keV dominates the region. Usually it is the most intense line in the spectrum. It has a contribution from ^{241}Am that becomes about 1% (relative) after 4 years. Because this line is from ^{237}U, we can only use it for aged samples. Its strength and freedom from nearby interference make it a good peak to use for shape and energy calibrations for analysis methods using peak fitting or response functions. For

TABLE VII

PEAK ENERGIES AND INTENSITIES IN 160-keV REGION[8]

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s•g)
^{239}Pu	158.100	1.000 E - 08	10.00	2.2942 E + 01
^{241}Pu	159.955	6.740 E - 08		2.5776 E + 05
^{239}Pu	160.190	6.200 E - 08	20.00	1.4224 E + 02
^{240}Pu	160.280	4.020 E - 06	0.70	3.3756 E + 04
^{239}Pu	161.450	1.200 E - 06	0.40	2.7530 E + 03
$^{237}U^{a}$	164.580	4.526 E - 07	0.50	1.7311 E + 06
^{241}Am	164.580	6.670 E - 07	3.00	8.4410 E + 04
	165.930	2.320 E - 07	4.00	2.9360 E + 04

[a]Uranium-237 activity computed assuming ^{241}Pu-^{237}U equilibrium. Uranium-237 branching ratio includes 2.46×10^{-5} ^{241}Pu alpha branch to ^{237}U.

TABLE VIII

COMPONENTS OF 160-keV COMPLEX

Isotope	Wt%	Percentage of 160-keV Complex from Indicated Isotope
239	93.5	4.5%
240	6.0	69.1%
241	0.3	26.4%
239	86.0	1.5%
240	12.0	50.4%
241	1.5	48.1%
239	67.0	0.3%
240	20.0	24.6%
241	8.0	75.1%

mixed oxides, ^{235}U peaks at 202.1 and 205.3 keV can interfere with the 203.54-keV ^{239}Pu line. The $^{239}Pu/^{241}Pu$ ratio formed with the 203.54/208.00 line pair gives best results for low-burnup material. For higher-burnup samples, the long tail from the very strong 208.00-keV ^{237}U peak hurts the weaker 203.54-keV ^{239}Pu peak. High ^{241}Am (~1%) content can cause a few tenths percent interference with the 203.5-keV peak. Table IX lists and Fig. 10 displays the parameters and spectral features of this region.

G. 332-keV Region

This region has contributions from ^{241}Pu-^{237}U, ^{241}Am, and ^{239}Pu as shown in Table X and Fig. 11. For high-burnup, aged material, the ratio of the 345.01-keV ^{239}Pu line to the 332.35-keV ^{241}Pu-^{237}U is useful for the $^{239}Pu/^{241}Pu$ ratio. Both the 332.35- and 335.40-keV lines from ^{241}Pu-^{237}U show very close interferences from ^{239}Pu peaks. In Fig. 11 the top plot of a very-low-burnup sample (98% ^{239}Pu) illustrates how close these two interferences are. For high-burnup material these ^{239}Pu interferences are fairly small. Table XI gives their relative magnitude for different isotopic compositions. After the ^{239}Pu interferences are removed, the two peak complexes retain both ^{241}Pu-^{237}U and ^{241}Am components. These can be used to obtain the $^{241}Pu/^{241}Am$ ratio.[3] Possible analysis methods for this region are peak fitting, response functions, and stripping.

TABLE IX
PEAK ENERGIES AND INTENSITIES IN 208-keV REGION[8]

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s•g)
^{239}Pu	203.537	5.600 E - 06	0.20	1.2847 E + 04
^{241}Am	203.870	2.900 E - 08	6.00	3.6700 E + 03
$^{237}U^{a}$	208.000	5.338 E - 06	0.20	2.0415 E + 07
^{241}Am	208.000	7.910 E - 06	0.50	1.0010 E + 06

[a] Uranium-237 activity computed assuming ^{241}Pu-^{237}U equilibrium.

Uranium-237 branching ratio includes 2.46×10^{-5} ^{241}Pu alpha branch to ^{237}U.

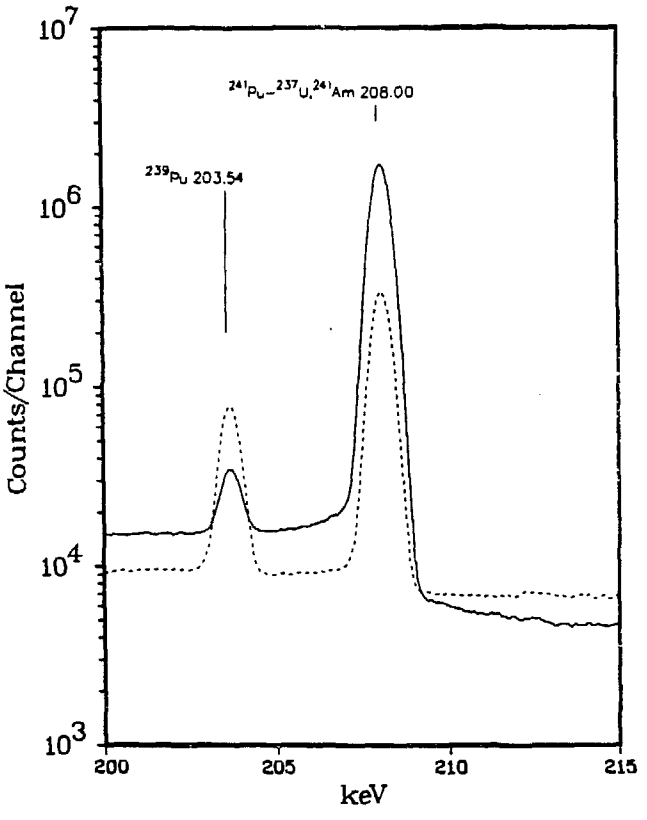

Fig. 10. Top (solid line)--PuO_2 counted with a 200-mm^2 by 10-mm-deep planar HpGe detector with resolution of 490 eV at 122 keV. Isotopic composition (wt%): 238, 0.0378%; 239, 78.89%; 240, 15.28%; 241, 4.42%; 242, 1.04%; ^{241}Am, 14 300 µg/g Pu.

Bottom (dashed line)--same as top with isotopic composition (wt%): 238, 0.016%; 239, 93.51%; 240, 6.15%; 241, 0.28%; 242, 0.039%; ^{241}Am, 480 µg/g Pu.

H. 375-keV Region

This region, shown in Fig. 12 and Table XII, has components from the same isotopes as the 332-keV region, ^{241}Pu-^{237}U, ^{241}Am, and ^{239}Pu. For all isotopes except ^{239}Pu, the branching ratios are lower than in the 332-keV region, so the isotopic information will be less precise. The strong 375.04-keV ^{239}Pu peak is often used for relative efficiency determination. The ^{241}Am interference at 376.59 keV becomes bothersome for concentrations above a few thousand µg/g Pu.

TABLE X

PEAK ENERGIES AND INTENSITIES IN 332-keV REGION

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s•g)
^{237}U[a]	332.354	2.977 E - 07	0.30	1.1384 E + 06
^{241}Am	332.354	1.490 E - 06	0.30	1.8856 E + 05
^{239}Pu	332.838	5.060 E - 06	0.20	1.1608 E + 04
^{237}U[a]	335.405	2.386 E - 08	1.00	9.1258 E + 04
^{241}Am	335.405	4.960 E - 06	0.30	6.2769 E + 05
^{239}Pu	336.107	1.134 E - 06	0.30	2.6016 E + 03
^{241}Am	337.720	4.290 E - 08	5.00	5.4290 E + 03
^{237}U[a]	337.750	2.189 E - 09	5.00	8.3732 E + 03
	340.450	4.059 E - 10	20.00	1.5523 E + 03
^{239}Pu	341.510	6.620 E - 07	0.40	1.5187 E + 03
	345.014	5.592 E - 06	0.20	1.2829 E + 04

[a] Uranium-237 activity computed assuming ^{241}Pu–^{237}U equilibrium. Uranium-237 branching ratio includes 2.46×10^{-5} ^{241}Pu alpha branch to ^{237}U.

I. 640-keV Region

This is the only region above 160 keV that we can use to measure ^{240}Pu. To use this region for ^{240}Pu, large samples are needed because of the low intensity of the 642.48-keV ^{240}Pu gamma ray. Nearby interferences from ^{239}Pu and especially ^{241}Am at 641.42 keV complicate the region. The 662.42-keV line of ^{241}Am provides a good peak for americium measurements, as does the 645.97-keV line for ^{239}Pu. The other gamma rays in the region are not generally used but have to be taken into account for peak-fitting or response-function analysis.

A large-volume coaxial detector (10% relative efficiency or greater) should be used in this region; hence, analysis schemes that analyze data from this region as well as the 100- to 400-keV region may choose to use two detectors.[19]

332-keV Region

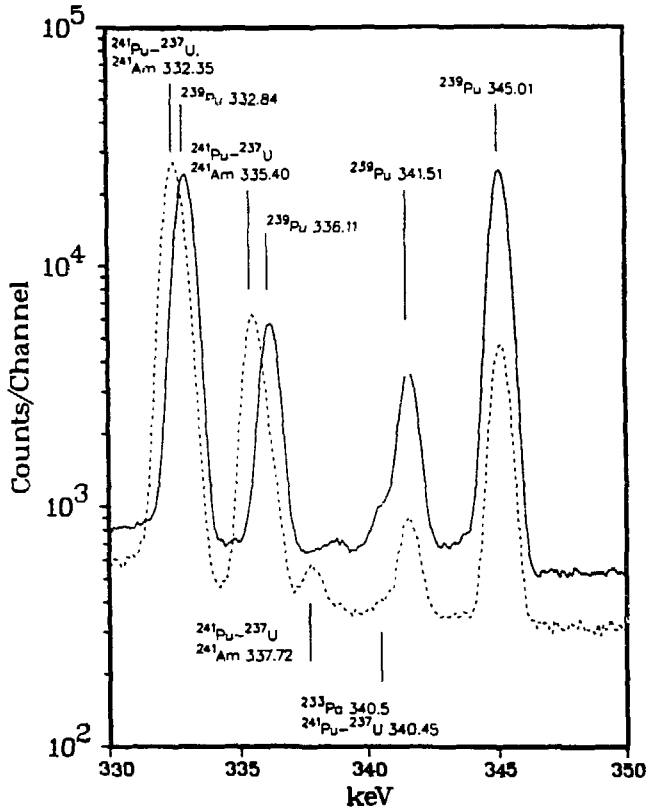

Fig. 11. Top (solid line)--PuO_2 counted with a 200-mm^2 by 10-mm-deep planar HpGe detector with resolution of 490 eV at 122 keV. Isotopic composition (wt%): 238, 0.0024%; 239, 97.96%; 240, 2.01%; 241, 0.020%; 242, 0.0030%; ^{241}Am, 11 µg/g Pu.

Bottom (dashed line)--same as top with isotopic composition (wt%): 238, 0.378%; 239, 78.89%; 240, 15.28%; 241, 4.42%; 242, 1.04%; ^{241}Am, 14 300 µg/g Pu.

If common fission products, for example, ^{95}Zr–^{95}Nb and ^{137}Cs, are in the sample, the region may become useless for analysis. A level as low as 10 µCi/g Pu is sufficient to negate useful information from this region.

Figure 13 and Table XIII display this region. We have offset the data plots in Fig. 13 for clarity.

TABLE XI

COMPONENTS OF 332- AND 336-keV COMPLEXES (^{241}Am NEGLECTED)

Isotope	wt%	Percentage of 332-keV Complex from Indicated Isotope	Percentage of 336-keV Complex from Indicated Isotope
239	93.5	76.1%	89.9%
241	0.3	23.9%	10.1%
239	86.0	36.9%	62%
241	1.5	63.1%	38%
239	67.0	7.9%	19.3%
241	8.0	92.1%	80.7%

IV. MEASUREMENT PRINCIPLES

A. Isotopic Ratio/Measurement

In general terms we can write the photopeak counts of a specific gamma ray from a given isotope emitted from a sample of arbitrary configuration as

$$C(E_j^i) = \lambda^i N^i BR_j^i \varepsilon(E_j) \quad , \tag{1}$$

where

$C(E_j^i)$ = photopeak area of gamma ray j with energy E_j emitted from isotope i,

λ^i = decay constant of isotope i, $\lambda^i = \ln 2/T_{1/2}^i$ (where $T_{1/2}^i$ is the half-life of isotope i),

N^i = number of atoms of isotope i,

BR_j^i = branching ratio (gamma rays/disintegration) of gamma ray j from isotope i, and

$\varepsilon(E_j)$ = total efficiency for photopeak detection of gamma ray with energy E_j. This includes detector efficiency, geometry, sample self-absorption, and attenuation in materials between the sample and detector.

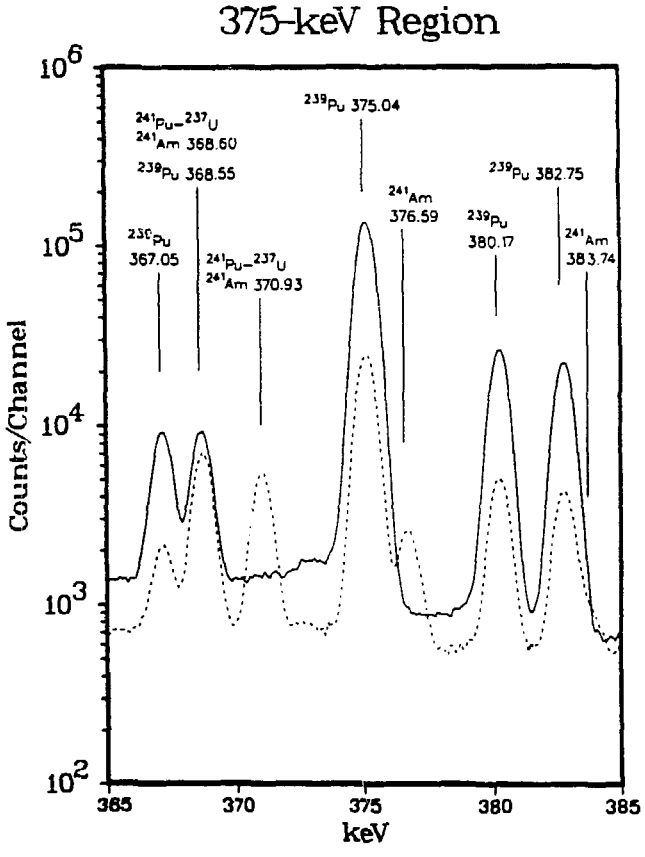

Fig. 12. Top (solid line)--PuO_2 counted with a 200-mm^2 by 10-mm-deep planar HpGe detector with resolution of 490 eV at 122 keV. Isotopic composition (wt%): 238, 0.0024%; 239, 97.96%; 240, 2.01%; 241, 0.020%; 242, 0.0030%; ^{241}Am, 11 µg/g Pu.

Bottom (dashed line)--same as top with isotopic composition (wt%): 238, 0.378%; 239, 78.89%; 240, 15.28%; 241, 4.42%; 242, 1.04%; ^{241}Am, 14 300 µg/g Pu.

In an analogous fashion we can write the count rate in terms of the mass of the isotope present as

$$C(E_j^i) = M_j^i \gamma_j^i \varepsilon(E_j) \quad , \tag{2}$$

where

M^i = mass of isotope i (g) and

γ_j^i = photon emission rate of gamma ray j from isotope i (gammas/s•g isotope).

TABLE XII

PEAK ENERGIES AND INTENSITIES IN 375-keV REGION[8]

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s•g)
^{239}Pu	367.050	8.650 E - 07	0.30	1.9844 E + 03
	368.550	9.030 E - 07	0.30	2.0716 E + 03
^{237}U[a]	368.605	1.055 E - 08	2.00	4.0360 E + 04
^{241}Am	368.605	2.170 E - 06	0.30	2.7462 E + 05
^{237}U[a]	370.934	2.713 E - 08	1.40	1.0377 E + 05
^{241}Am	370.934	5.230 E - 07	0.80	6.6186 E + 04
^{239}Pu	375.042	1.570 E - 05	0.10	3.6018 E + 04
^{241}Am	376.595	1.383 E - 06	0.70	1.7502 E + 05
^{239}Pu	380.166	3.051 E - 06	0.20	6.9995 E + 03
	382.751	2.587 E - 06	0.20	5.9350 E + 03
^{241}Pu	383.740	2.820 E - 07	1.50	3.5687 E + 04

[a]Uranium-237 activity computed assuming ^{241}Pu-^{237}U equilibrium. Uranium-237 branching ratio includes 2.46 x 10^{-5} ^{241}Pu alpha branch to ^{237}U.

We may rearrange these two equations to give expressions for the atom ratio of two isotopes from Eq. (1) and the mass ratio of two isotopes from Eq. (2).

The atom ratio of isotope i to isotope k from measurement of a gamma ray with energy E_j from isotope i and E_ℓ from isotope k is given by

$$\frac{N^i}{N^k} = \frac{C(E_j^i)}{C(E_\ell^k)} \times \frac{T_{1/2}^i}{T_{1/2}^k} \times \frac{BR_\ell^k}{BR_j^i} \times \frac{RE(E_\ell)}{RE(E_j)} \quad . \tag{3}$$

The similar expression for the mass ratio is

$$\frac{M^i}{M^k} = \frac{C(E_j^i)}{C(E_\ell^k)} \times \frac{\gamma_\ell^k}{\gamma_j^i} \times \frac{RE(E_\ell)}{RE(E_j)} \quad . \tag{4}$$

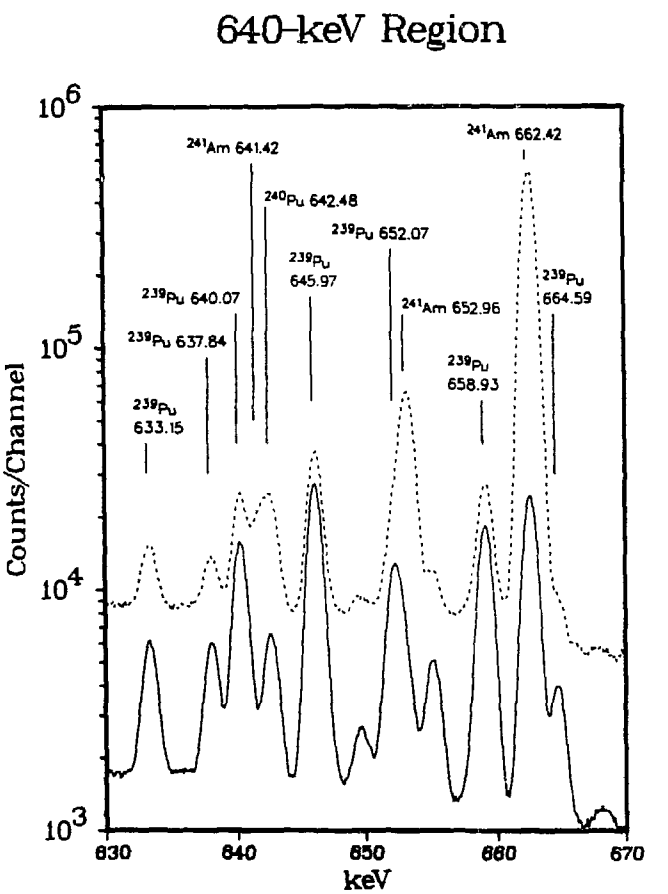

Fig. 13. Top (dashed line)--530 g plutonium as PuO_2 counted with 10.2% relative efficiency coaxial HpGe detector with 1.65-keV resolution at 1332 keV. Isotopic composition (wt%): 238, 0.302%; 239, 82.49%; 240, 13.75%; 241, 2.69%; 242, 0.76%; ^{241}Am, 11 800 µg/g Pu.

Bottom (solid line)--500 g plutonium metal, counted with 11.7% relative efficiency coaxial HpGe detector with 1.75-keV resolution at 1332 keV. Isotopic composition (wt%): 238, 0.012%; 239, 93.82%; 240, 5.90%; 241, 0.240%; 242, 0.028%; ^{241}Am, 630 µg/g Pu.

In Eqs. (3) and (4), the total efficiency has been rewritten in terms of the relative efficiency RE. Geometry factors cancel, and the ratio of efficiencies (relative efficiency) at energies E_ℓ and E_j includes sample self-absorption, attenuation in materials between the sample and detector, and detector efficiency. The half-lives, $T_{1/2}$; branching ratios, BR; and photon

TABLE XIII

PEAK ENERGIES AND INTENSITIES IN 640-keV REGION[8]

Isotope	Energy (keV)	Branching Ratio (photons/dis)	Error (%)	Activity (photons/s•g)
^{241}Am	633.000	1.260 E - 08	15.00	1.5945 E + 03
^{239}Pu	633.150	2.530 E - 08	1.20	5.8042 E + 01
	637.837	2.560 E - 08	1.20	5.8730 E + 01
	640.075	8.200 E - 08	0.60	1.8812 E + 02
^{241}Am	641.420	7.100 E - 08	4.00	8.9851 E + 03
^{240}Pu	642.480	1.245 E - 07	1.00	1.0454 E + 03
^{239}Pu	645.969	1.489 E - 07	0.40	3.4160 E + 02
	649.321	7.120 E - 09	7.00	1.6334 E + 01
	650.529	2.700 E - 09	15.00	6.1942 E + 00
	652.074	6.550 E - 08	0.60	1.5027 E + 02
^{241}Am	652.960	3.770 E - 07	2.00	4.7710 E + 04
^{239}Pu	654.880	2.250 E - 08	1.20	5.1618 E + 01
	658.929	9.690 E - 08	0.70	2.2230 E + 02
^{241}Am	662.420	3.640 E - 06	0.30	4.6065 E + 05
^{239}Pu	664.587	1.657 E - 08	1.60	3.8014 E + 01
	668.200	3.930 E - 10	30.00	9.0160 E - 01

emission rates are either known nuclear data or can be calculated from known nuclear data.

The C(E) are measured, leaving only the ratio of efficiencies to be determined. The need for nothing more than an efficiency ratio removes the problems associated with the geometrical reproducibility associated with absolute measurements and makes the method applicable to samples of arbitrary size, shape, and composition.

For every sample, we can determine the ratio of the relative efficiency at selected energies from the measured spectrum of that sample. Looking at Eq. (1) and considering a series of gamma-ray lines from a single isotope, we

see that the quotient of the photopeak counts at energy E_j^i and the branching ratio BR_j^i is proportional to the efficiency at energy E_j.

$$\frac{C(E_j^i)}{BR_j^i} \propto \varepsilon(E_j) \quad . \tag{5}$$

Thus, this quotient can define the shape of the relative efficiency for that sample measurement. In an analogous fashion, we could use Eq. (2) to define the relative efficiency by replacing BR_j^i in Eq. (5) with γ_j^i. Because ratios are used, all that is important is the shape of the curve.

With a series of points from a single isotope defining the shape of the relative efficiency curve, we can apply curve-fitting techniques[16] to define the relative efficiency at an arbitrary energy or simply interpolate between measured points. To better define the shape of these relative efficiency curves, we can use points from more than one isotope by normalizing one isotope to another.[16,17] Gamma rays from ^{239}Pu and ^{241}Pu–^{237}U are most often used to define the relative efficiency curves in the range from 130 to 450 keV.

Measuring isotopic ratios for closely spaced gamma rays from different isotopes is advantageous because relative efficiency ratios will be near unity. However, even for closely spaced lines in the 120- to 200-keV region, we cannot neglect this correction. A typical correction for the 152.7-keV ^{238}Pu/148.6-keV ^{241}Pu ratio can be 10%.

After appropriate isotopic ratios are measured, it is usually desirable to combine them to produce isotopic fractions. First, we must convert all measured ratios to a common denominator, say ^{241}Pu for the purpose of illustration. Then, neglecting ^{242}Pu, we observe

$$1 = f_{238} + f_{239} + f_{240} + f_{241} \quad , \tag{6}$$

where f_i is the isotopic fraction of isotope i.

Dividing by f_{241} we get

$$\frac{1}{f_{241}} = \frac{f_{238}}{f_{241}} + \frac{f_{239}}{f_{241}} + \frac{f_{240}}{f_{241}} + 1 \quad , \tag{7}$$

giving an expression for the isotopic fraction of ^{241}Pu (f_{241}) in terms of the three measured ratios f_{238}/f_{241}, f_{239}/f_{241}, and f_{240}/f_{241}. We obtain the remainder of the isotopic fractions from

$$f_i = f_{241} \times \left[\frac{f_i}{f_{241}}\right] \quad , \tag{8}$$

where i = 238, 239, and 240.

Section V.C discusses the incorporation of ^{242}Pu into this analysis. If the ratio of ^{241}Am to any of the plutonium isotopes (usually ^{239}Pu) has been measured, we find the absolute fraction of ^{241}Am by

$$f_{Am} = f_i \times \frac{f_{Am}}{f_i} \quad . \tag{9}$$

Note that this gives the weight or atom fraction of ^{241}Am in the sample with respect to total plutonium, not total sample.

For this method to work, the plutonium in the sample must be isotopically homogeneous even though it may be physically and geometrically inhomogeneous. This restriction also applies to the ^{241}Am in the sample. The Am/Pu ratio must be uniform throughout all of the plutonium in the sample.

B. Absolute Isotopic Mass Measurement

While the ratio method discussed in Sec. IV.A can be applied to arbitrary samples, a more specialized method has also been used in the case of samples with reproducible geometries. Gunnink and coworkers[4,11,15] have used the

method of absolute measurement of the amount of each isotope in the solution samples. This method depends upon the equation

$$C(E_j^i) = K_j^i \, m^i \quad , \tag{10}$$

with

$C(E_j^i)$ = photopeak area of gamma ray j with energy E_j emitted from isotope i,

m^i = mass of isotope i in sample, and

K_j^i = calibration constant for gamma ray j from isotope i.

This technique uses direct calibration with standard samples identical in geometry to the unknowns to determine the calibration constants. Self-attenuation corrections may be needed to account for differences between calibration standards and unknowns. Given the amount of each isotope in the sample, we obtain the isotopic fractions from

$$f_i = \frac{m_i}{\sum_{i=238}^{241} m_i} \quad . \tag{11}$$

For these measurements, the size and shape of the samples are carefully chosen to minimize (but not eliminate) self-absorption corrections. This is an example of the sample being made to fit the method rather than vice versa. We next discuss application of ^{242}Pu correlation techniques to this procedure and ratio methods.

C. ^{242}Pu Isotopic Correlation

Section II.C mentioned that ^{242}Pu cannot be measured directly because of its low activity, low abundance, and weak gamma rays. Instead, given knowledge of the other isotopic fractions in the sample, we use isotopic correlation[7] techniques to predict the ^{242}Pu abundance. It is well known that correlations exist among the plutonium isotopic abundances. These correlations

arise from the isotope production process. These correlations depend upon the reactor type and details of the plutonium's irradiation history, so it is difficult, if not impossible, to find a single correlation that is optimum for all material. Gunnink[7] suggests a correlation of

$$242 = \frac{K\ (240)(241)}{(239)^2} \tag{12}$$

as being linear and relatively independent of reactor type. In Eqs. (12) and (13), the isotope mass number represents the isotopic fraction of that isotope. This correlation applies at reactor discharge time. Gunnink finds a best-fit constant K to have a value of 52 when the isotopes are given in weight percent. One disadvantage to this correlation is its dependence on ^{241}Pu, which decreases in absolute abundance by about 5% per year. To make best use of this correlation we must correct the ^{241}Pu abundance to reactor discharge time. Often this time is not known, but we can make a partial correction, back to the last chemical separation, by adding the ^{241}Am ingrowth back to the ^{241}Pu content before computing the correlation.

A correlation not involving ^{241}Pu has been suggested;[7,20]

$$242 = \frac{K(240)^3}{(239)^2} \quad . \tag{13}$$

This correlation is linear for a given reactor type, but the slope K depends upon the specific reactor.

Once the isotopic fraction of ^{242}Pu has been found using a suitable correlation, known values, or stream averages, the other measured isotopic fractions are corrected by

$$f_i^c = f_i\ (1-f_{242}) \quad , \tag{14}$$

where

f_i^c = normalized isotopic fractions including ^{242}Pu and

f_i = normalized isotopic fractions without ^{242}Pu.

This preserves the normalization condition that the isotopic fractions sum to unity.

V. DATA ACQUISITION

A. Electronics

Plutonium isotopic measurements use conventional, high-quality, nuclear instrumentation module (NIM) type electronics. Several manufacturers provide excellent modules. Methods using fixed ROI or response-function methods for obtaining peak areas require digital gain and zero stabilization . A bias supply suitable for a high-resolution germanium detector and an amplifier with baseline restoration, pileup rejection, and time constants in the 1- to 6-μs range are required. Other modules often used are liquid-nitrogen-level monitors, scalers or rate meters to monitor detector count rates, and oscilloscopes to aid in setup and troubleshooting.

Most methods require a multichannel analyzer (MCA) with a 4-k channel memory. Two-detector systems require two analog-to-digital converters and 8-k memory to divide between the two detectors.

The extensive data analysis requirements dictate that the MCA interface with a computer. Sixteen-bit minicomputers with a 32-k word memory are adequate. A disk is needed for program and data file storage. Simple analysis can be done with programmable calculators once peak areas are obtained.

B. Detectors

All data analysis methods benefit from the the best possible resolution and peak shape. These criteria are the most important parameters when considering a detector for a plutonium isotopic system. The most common detectors are planar HpGe detectors with a common size being 200 mm^2 by 10-13 mm deep, which gives a good tradeoff between resolution and efficiency. Resolutions of <500 eV at 122 keV are commercially available with this size detector. A peak shape specification of 2.55 or better for the ratio of full width at one-fiftieth maximum to full width at half maximum (FWHM) at 122 keV will help ensure good peak shape. Good detectors give values of below 2.5 for this parameter with no background subtraction. Planar detectors can be used up to 400 keV. High-quality coaxial detectors can be used in the 100- to 400-keV region, but they do worsen the problem of partially resolved peaks for methods using ROI summation techniques.

For measurements in the 600-keV region, a coaxial detector is better because the planar efficiency is too low. Ten percent relative efficiency is adequate, and bigger detectors can profitably be used. Again, resolution is important. The very best resolution may negate the need to peak fit the entire 600-keV region.[16] Resolutions of 1.7 keV or better at 1332 keV are available.

Detector geometry may be either uplooking or sidelooking. The physical constraints of the measurement area often dictate the geometry.

C. Filters

Filtering is required to reduce the count rate from the 59.54-keV ^{241}Am line that dominates any unfiltered spectrum from an aged sample. If left unfiltered, the americium peak will cause unnecessary deadtime and will sum with x rays and gamma rays in the 100-keV region to produce interferences in the 150- to 165-keV region. A thickness of 0.060 in. (0.15 cm) of either lead or cadmium will attenuate a 60-keV gamma ray by a factor of over 1000. A graded filter will suppress x rays from the main filter, with 0.010 in. (0.025 cm) of copper suppressing cadmium K x rays at 22 keV by a factor of 100. Lead x rays (72-87 keV) from shielding often appear in the spectrum. As much as 0.090 in. (0.23 cm) of cadmium is needed to suppress these.

A reasonable rule of thumb is to filter enough to reduce the peak height at 60 keV to less than those in the 100-keV region. Too much filtering will unnecessarily reduce the intensity of the peaks in the 120- to 200-keV range (see Sec. III.C). Trial-and-error experiments with high-americium content samples are usually necessary to see if filtering is sufficient. The region between 153 and 160 keV should be flat.[19]

Little, if any, filtering is needed for freshly separated samples (no ^{241}Am or ^{237}U) when using the 100-keV region or the 40-keV region.

D. Sample Considerations

Methods designed for arbitrary sample configurations do not have geometry or positioning requirements. One uses distance or collimation to tailor the count rate. Count rates are kept reasonably low to maximize resolution and usually fall in the 5- to 15-kHz range. Developments in high-count-rate spectroscopy[21,22] hold the promise of increasing this range significantly.

There is a current trend to higher counting rates and shorter shaping times to obtain more throughput for methods relying on the analysis of gamma

rays above 120 keV. These higher-count-rate methods still use conventional electronics operating with shorter time constants (~1 μs) that reduce deadtime and pileup losses. Rates up to 50 kHz are reasonable with throughput increases by approximately a factor of 3 over a 3-μs, 15-kHz measurement. These higher counting rates do worsen the system resolution. One must be certain that the chosen analysis method is robust enough to handle the poorer resolution.

Measurements on solutions usually use a fixed-sample geometry with a disposable sample vial or a fixed, refillable sample cell. The cell thickness is usually tailored to the sample concentration range and the energy range to minimize the attenuation corrections needed for absolute counting methods.

Coincidence summing effects may be present if small samples are placed close to the detector.[18] Experimenters have noted an effect of 1.6% for 3- to 4-cm sample distance with the use of a planar detector for the 129 + 203 keV = 332-keV lines from ^{239}Pu. Bulk samples will generally be farther away, making this effect less important.

The analysis schemes described previously require that the plutonium be isotopically homogeneous and that the americium/plutonium ratio be uniform if americium measurements are desired. If the homogeneity requirements are satisfied, the sample need not be rotated. If the homogeneity requirements are not satisfied, rotation will still not ensure a correct answer, but it can reduce errors in most cases.

Common electrochemical processes produce residues such as slag, crucibles, and salts in which there may be a physical segregation of the plutonium and americium. For samples where the correct americium content is needed for calorimetry measurements, the arbitrary sample methods described previously will not be accurate. Current research[23] has led to an analysis method that corrects for inhomogeneous americium/plutonium content by using a separate relative efficiency curve for americium peaks. One should validate this method for the specific sample types to be measured because results can be dependent on the sample size and composition.

Bulk samples (containing kilogram quantities of plutonium) have high neutron emission rates (10^5 to 10^6 n/s). Long exposure to large samples can cause neutron damage to the detector. Detector performance may significantly deteriorate in one year of heavy usage. With this in mind, controlling the count rate by increasing the sample-to-detector distance or by opening up the

collimation becomes desirable as opposed to tightening collimation or decreasing the sample distance. One wishes to use the greatest sample-to-detector distance consistent with count-rate requirements to decrease the neutron flux at the detector. In addition, neutron interactions in the detector increase the continuum under the photopeaks, which worsens the measurement precision.

E. Counting Time

The counting time required to produce accountability-quality isotopic precision is a function of the spectral region studied. In the 40- and 100-keV regions, counting times of 1000 s to 1 h are usually satisfactory. For bulk samples of arbitrary geometry using gamma rays above 120 keV, counting times of 1 or 2 h or longer are necessary and still do not produce as good a precision as shorter times in the lower-energy regions. For larger samples, simple verification of the $^{239}Pu/^{241}Pu$ ratio may take only a few minutes. Some specific examples will be discussed in Sec. VII.

VI. DATA ANALYSIS

The general term data analysis can refer both to the method used to extract the photopeak areas and to the method used to combine the photopeak areas to obtain the required isotopic information. Below we will describe several of the methods and techniques used in systems that have been implemented in the United States. We do not wish to ignore methods used elsewhere but instead are attempting to concentrate on describing methods with which we are most familiar.

A. ROI Summation

This is the simplest method for extracting peak areas.[24] Most MCAs feature a built-in form of this analysis. The background under the peak is determined using the average count in background regions defined above and below the peak of interest. Several methods are often used. The average background from the two ROIs (zero-slope line) can be used. A sloping linear background between the centroids of the ROIs is another option. It gives the same results as the zero-slope average if the background ROIs are symmetric about the peak ROI. A smoothed step-function[25] background, also common, probably provides the most physically realistic estimate for cases where the background does not have a positive slope.

The smoothed step function has the form

$$B_i = b_n + (b_m - b_n) \sum_{j=n}^{j=i} Y_j \Big/ \sum_{k=n}^{k=m} Y_k \quad , \tag{15}$$

where

B_i = computed background in channel i,

Y_i = gross spectrum count in channel i,

b_n = average background count in low-energy background ROI, and

b_m = average background count in high-energy background ROI.

One should also subtract the high-energy background b_m from the gross spectrum Y before computing Eq. (15).

Needless to say, the ROI summation method works best for single isolated peaks. Indeed, there is little or no reason to do anything else to get the peak area of a single isolated peak. Overlapping peaks, for example, 125-, 160-, 332-, and 375-keV regions, are a different story. ROI summation can be used to get the area of multiplets, but one must isolate the individual components by an integral stripping method using neighboring peaks and known relative efficiency differences. This analysis generally leads to a loss of precision.

Stabilizers are required to keep peaks within their fixed ROIs, and background windows must be chosen carefully to avoid contaminate peaks, for example, weak ^{241}Am peaks from high-americium-concentration samples.

The main advantage of ROI summation is that it is easy to implement, understand, and use.

B. Peak Fitting

Peak-fitting techniques have been in use in gamma-ray spectroscopy for decades. Techniques[26] developed by Gunnink and coworkers at Livermore are widely used both for plutonium isotopic measurements and in other gamma-ray spectroscopy areas. The GRPANL[27] code has been automated at the Mound Facility[28] and forms the basis for the GRPAUT[16] program used there.

This code fits a background-subtracted photopeak with a Gaussian function plus exponential tailing functions as

$$Y_i = Y_o\{\exp[\alpha(X_i - X_o)^2] + T(X_i)\} \quad , \tag{16}$$

with

Y_i = net counts in channel X_i for a single peak,
Y_o = peak height at centroid ($X_i = X_o$),
$\alpha = -4\ \ell n2/(FWHM)^2 = -1/2\sigma^2$ with σ being the standard deviation of the Gaussian,
X_o = peak centroid, and
$T(X_i)$ = tailing function at channel X_i.

The tailing function is given by

$$T(X_i) = \{A \exp[B(X_i - X_o)] + C \exp[D(X_i - X_o)]\}$$

$$\{1 - \exp[0.4\ \alpha(X_i - X_o)^2]\}\delta \quad , \tag{17}$$

where

A and C = short- and long-term tailing amplitude,
B and D = short- and long-term tailing slope, and
$\delta = 1$ for $X_i < X_o$; $\delta = 0$ for $X_i \geq X_o$.

The right-hand bracket brings the tailing function smoothly to zero at the peak centroid shown in Fig. 14. For many applications we can neglect the long-term tail (C = 0); however, for large multiplets with strong peaks, including it is desirable.

Each peak can have as many as seven parameters, Y_o, X_o, α, A, B, C, and D, with the peak position X_o and peak height Y_o generally being the principal parameters of interest. Fortunately, we can predetermine many of the other parameters.

The FWHM (related to α) can be determined as a function of gamma-ray energy E as

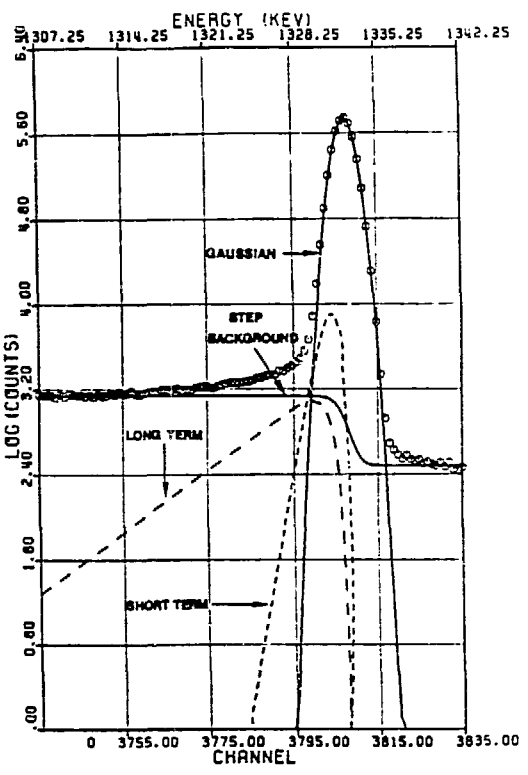

Fig. 14. Gamma-ray photopeak obtained with Ge(Li) detector showing (1) Gaussian, (2) short-term tailing, (3) long-term tailing, and (4) diffused-step background contributions to spectral peak shape.[28]

$$FWHM^2 = k_1 + k_2 E \quad . \qquad (18)$$

The measured widths of two peaks in the spectrum can be used to find k_1 and k_2, thus giving the FWHM value at any energy.

Experience[26] shows that the short-term tailing slope B is a constant for a given detector system. Measuring this for a high-energy peak where tailing is largest is desirable.

The short-term tailing amplitude A is given by

$$\ln A = k_3 + k_4 E \quad . \qquad (19)$$

Once the short-term slope B has been found, it is fixed, and then the short-term tail amplitude can be found from two peaks.

The GRPANL formalism also allows for the fitting of resolution-broadened x-ray peaks that have different intrinsic line shapes (Lorentzian) than do gamma rays.[29] Only by using this feature can we do accurate peak fitting in the 100-keV region.

Before the fitting, the step-function background algorithm of Eq. (15) is used to remove the background. Then an iterative, nonlinear least-squares technique[26,27] is used to fit the peak.

Various "tricks" can reduce the number of free parameters in the fitting process. For plutonium isotopics, the peak energies are known;[8] thus, positions of peaks in a multiplet may be fixed relative to one peak in the group. Because relative peak intensities from the same isotope are also known, these may be fixed, too.

Because the method is an iterative technique, data analysis times can be fairly long. The time depends upon the number of peaks and number of free parameters, as well as upon the type of computer and disk. A typical time for analysis of a plutonium spectrum from 120 to 450 keV with over 50 peaks in about 15 groups may be about 10 min on a PDP-11/23. This time is usually not significant when we consider that data accumulation times can be a factor of 10 longer.

C. Response-Function Analysis

This method uses the peak-fitting principles discussed above to calculate the shape of the detector response to a particular isotope in a particular energy region. With the shape of the response known, only the peak height or envelope height [Y_o in Eq. (16)] is unknown. The fitting problem is then reduced to a linear least-squares problem, which is quickly solved.

To carry out this type of analysis, the peak-shape characteristics of the detector must be predetermined or acquired from the spectrum of the sample under study. If the short-term tail slope B has been predetermined for the detector, then fitting two photopeaks (one low energy and one high energy) can give the variation of the FWHM with energy [Eq. (18)] and the variation of the short-term tail amplitude [A, Eq. (19)] with energy. We usually do this as part of premeasurement calibration and store these parameters in a data file to be used later. Long-term tail parameters, if used, are also determined at this time.

Differences in count rates between samples can affect the FWHM of the peaks. This can be accounted for by determining the FWHM of a low-energy peak in each spectrum, 60-keV ^{241}Am, for example, and adjusting the noise term, K_1 in Eq. (18), for the FWHM in E.

This procedure enables us to know all the shape parameters, energies, and peak positions for spectral lines in each spectrum. We can then compute the response profile for each isotope in the region to be fitted. For the 100-keV region that contains x rays, we use the formalism of Ref. 29 to compute the x-ray line shapes. Only linear equations are left to solve for the relative intensities of each isotope contributing to the region. Some counting situations can yield absolute intensities for the fitted data if previous calibrations exist.

This method has been used to fit the complex 100-keV region[4,11,15] and also for spectra in the 120- to 370-keV region.[30]

VII. IMPLEMENTED SYSTEMS

In this section we will describe some systems that have been put into routine use in the United States and their characteristics, accuracies, and precisions.

A. Rockwell-Hanford

The system in use at Rockwell-Hanford[31] probably has been used more than any other system for measuring solids. It uses four 300-mm^2 by 7-mm-deep planar HpGe detectors to measure oxides, metals, impure oxides, mixed oxides, and scrap. Figure 15 shows a photograph of two of the detectors. Data are taken from the MCA to an off-line computer for analysis. Ratio methods are used on peaks in the 120- to 400-keV range using the methods outlined in Ref. 3. Software is being updated based on more recent work.[16]

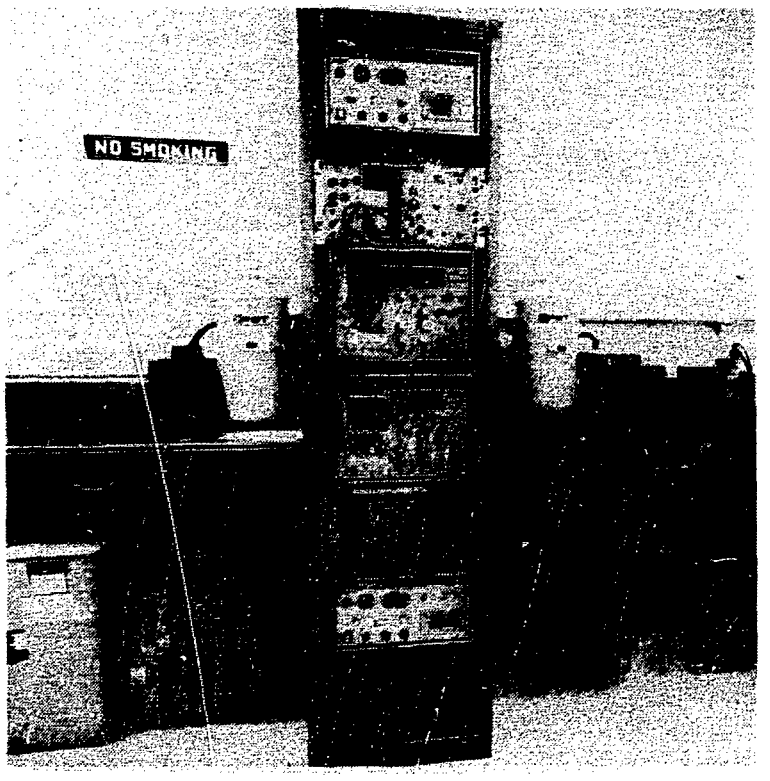

Fig. 15. Plutonium isotopic system implemented at Rockwell-Hanford. (Photo courtesy of R. A. Hamilton, Rockwell-Hanford.)

Samples are counted for 10 000 s at a count rate of 3000 Hz with the sample-to-detector distance adjusted to give the desired count rate. No sample rotation is used.

A large volume of performance data exists for this instrument on 14 standards spanning the range from 2% to 24% ^{240}Pu. The isotopic ratio expressions use only the fundamental branching ratios and half-lives. No bias corrections are made. Plutonium-242 is not calculated. Table XIV shows some of the performance data as they apply to the specific power used to interpret calorimetry.

Measurement precision for the specific power is in the 0.5% to 1.0% RSD range, with measurement bias being of the same order.

Plutonium isotopic measurement by gamma-ray spectroscopy is somewhat forgiving when used to compute the specific power. Biases in one isotopic fraction are partially cancelled by the normalization condition that all isotopes must sum to unity.

B. Los Alamos

The Plutonium Processing Facility at Los Alamos uses the basic methods of Ref. 3 as described in Refs. 17 and 32. Gain-stabilized data in the 120- to 400-keV region are acquired with 200-mm^2 by 13-mm-deep planar HpGe detectors at rates up to 20 kHz with time constants of 2 or 3 μs. Analysis is done on-line and has been applied to material with 2% to 18% ^{240}Pu and with ^{241}Am up to 2.0%. All ratios are measured with respect to ^{241}Pu, and Table XV tabulates the different ratios used for aged and freshly separated material. Peak areas are determined using simple ROI summation.

A correlation of the form of Eq. (12) ($242 = K \times 240 \times 241/239^2$) is used to compute ^{242}Pu. A constant with the value of 90 is used to give a result in weight percent for material with a wide variety of reactor histories.

Because ROI integration is used for peak areas, interfering peak areas must be subtracted using clean neighboring peaks. The 129.3-keV peak is used to subtract ^{239}Pu interferences from the 125-keV region. The 164.6-keV peak is used to subtract ^{241}Pu from the 160-keV complex for aged samples. The 161.5-keV ^{239}Pu peak is used to subtract the small ^{239}Pu interference from the 160-keV complex. At the 332-keV region, the 345-keV ^{239}Pu peak is used to remove interferences at 332.8 and 336.1 keV. The ^{241}Pu-^{237}U, ^{241}Am lines at 332.4 and 335.4 keV are used to compute the ^{241}Pu/^{241}Am ratio,[3] which is in

TABLE XIV

PERFORMANCE OF ROCKWELL-HANFORD ISOTOPICS SYSTEM FOR SPECIFIC POWER

Isotope	1(oxide)	2(metal)	3(oxide)	4(oxide)	5(oxide)	6(metal)	7(metal)
$\%^{238}Pu$	0.0063	0.0008	0.028	0.14	0.064	0.069	0.089
$\%^{239}Pu$	97.56	93.73	91.64	87.87	86.50	80.77	73.81
$\%^{240}Pu$	2.40	6.03	7.65	10.23	11.78	17.10	22.83
$\%^{241}Pu$	0.038	0.21	0.569	1.49	1.42	1.66	2.26
$\%^{241}Am$	0.059	0.138	0.447	1.26	0.088	1.12	2.13
No. of measurements	102	103	102	109	98	103	101
Precision of specific power (% RSD) calculated from measurement reproducibility	1.02%	0.72%	0.65%	0.55%	0.84%	0.62%	0.53%
Bias: Specific power from NDA divided by specific power from mass spectrometry values	0.9914	0.9921	1.003	1.008	1.016	1.002	1.028

TABLE XV

RATIOS USED IN LOS ALAMOS PLUTONIUM ISOTOPIC SYSTEM

Ratio	Aged		Freshly Separated
238/241	152.7/148.6 keV		152.7/148.6 keV
239/241	345.0/332.4 keV	Wtg Av	129.3/148.6 keV
	203.5/208.0 keV		
240/241	160.3/164.6 keV		160.3/148.6 keV
Am/239	125.3/129.3 keV	Wtg Av	125.3/129.3 keV[a]
	169.6/171.3 keV		

[a] Americium content is usually too low to measure.

turn used to correct ^{241}Pu-^{237}U peaks at 164.6, 208.0, 267.5, and 332.4 keV for their ^{241}Am content.

Relative efficiency is found from ^{239}Pu and ^{241}Pu-^{237}U lines normalized to each other. Simple linear and quadratic interpolation and extrapolation provide needed values. Figure 16 shows typical curves.

The simple ROI integration method can present problems in obtaining bias-free peak areas where there are close interferences, for example, 125 keV, 160 keV, and 332 keV. For this reason, each isotopic ratio is calibrated with standard samples allowing one calibration constant for each term in the isotopic ratio expression. Figure 17 shows the average accuracy of the system after such a calibration with a wide variety of samples, metal and oxide from <10.5 g Pu to ~1 kg Pu. If the standard deviation in Fig. 17 is taken as a measure of the accuracy for an arbitrary sample, then it appears to be better than 1% for ^{239}Pu, ^{240}Pu, and ^{241}Pu and a few percent (limited somewhat by standards) for ^{238}Pu and ^{241}Am.

Figures 18 and 19 show the precision for the isotopic fractions for two different burnups as a function of counting time. The isotopic fractions are listed by each curve. The predicted precision is that computed by the analysis program from propagated counting statistics. Figure 20 shows the precision of the specific power for the data shown in Figs. 18 and 19. It is better than 1% for count times longer than 30 min. For typical counting times of 2 h, specific power precision is about 0.5%.

Figure 21 shows the system with two detectors that can acquire data from two samples simultaneously. A sample platform above the detectors can be raised or lowered to tailor the count rate. The software will handle up to four detectors, so expansion up to four detectors can be accomplished by addition of only detectors and NIM electronics. This expansion has recently been completed. The single system can now acquire and analyze on-line data from four samples simultaneously.

C. Mound

The Mound Facility has been carrying out plutonium isotopic measurements in support of their calorimetry effort for some time. Mound researchers[28] have automated the GRPANL peak-fitting code[27] from Livermore to produce the GRPAUT[16] program for isotopic analysis. The peak-fitting procedure follows the description outlined in Sec. VI.B. Isotopic ratios are measured.

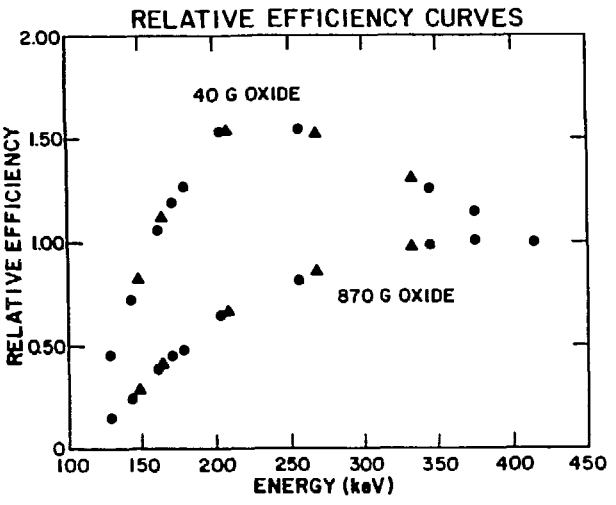

Fig. 16. Typical relative efficiency curves for two sample sizes with a 200-mm^2 by 10-mm-deep planar HpGe detector. Solid circles from ^{239}Pu. Triangles from ^{241}Pu and ^{241}Pu–^{237}U.

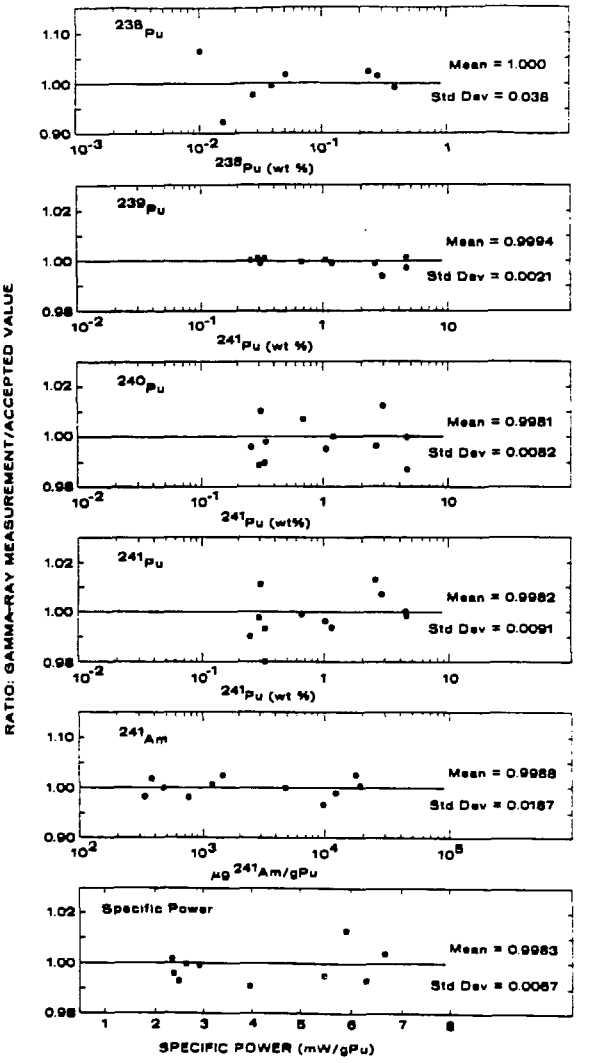

Fig. 17. Los Alamos plutonium isotopic system accuracy for a wide range of samples.

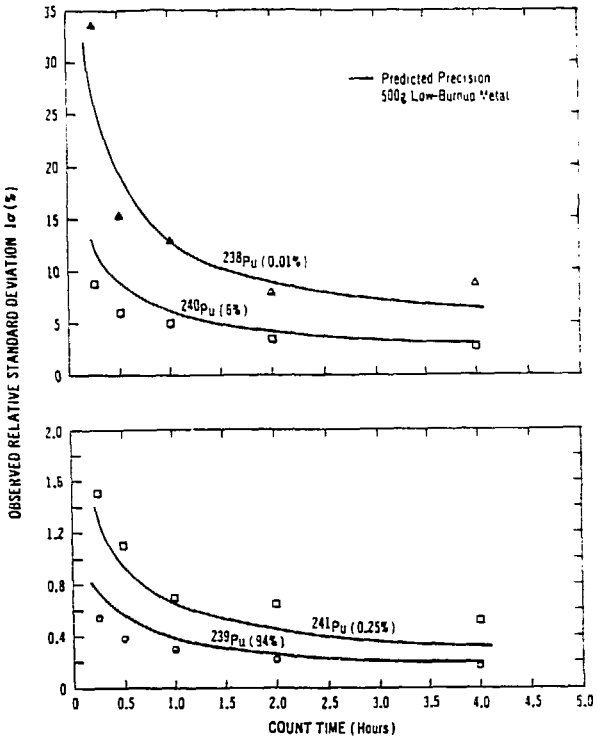

Fig. 18. Precision of isotopic fractions determined from 30 repeated measurements.

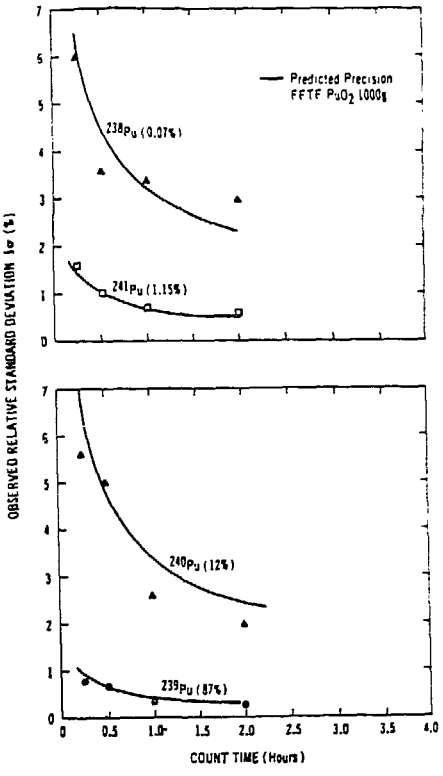

Fig. 19. Precision of isotopic fractions determined from 30 repeated measurements.

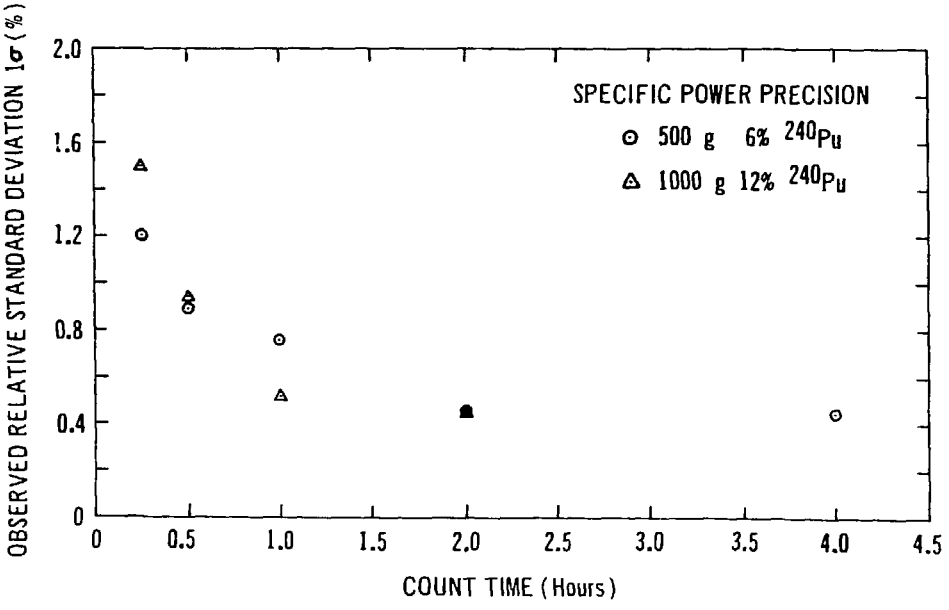

Fig. 20. Precision of specific power for 2 samples from 30 repeated measurements.

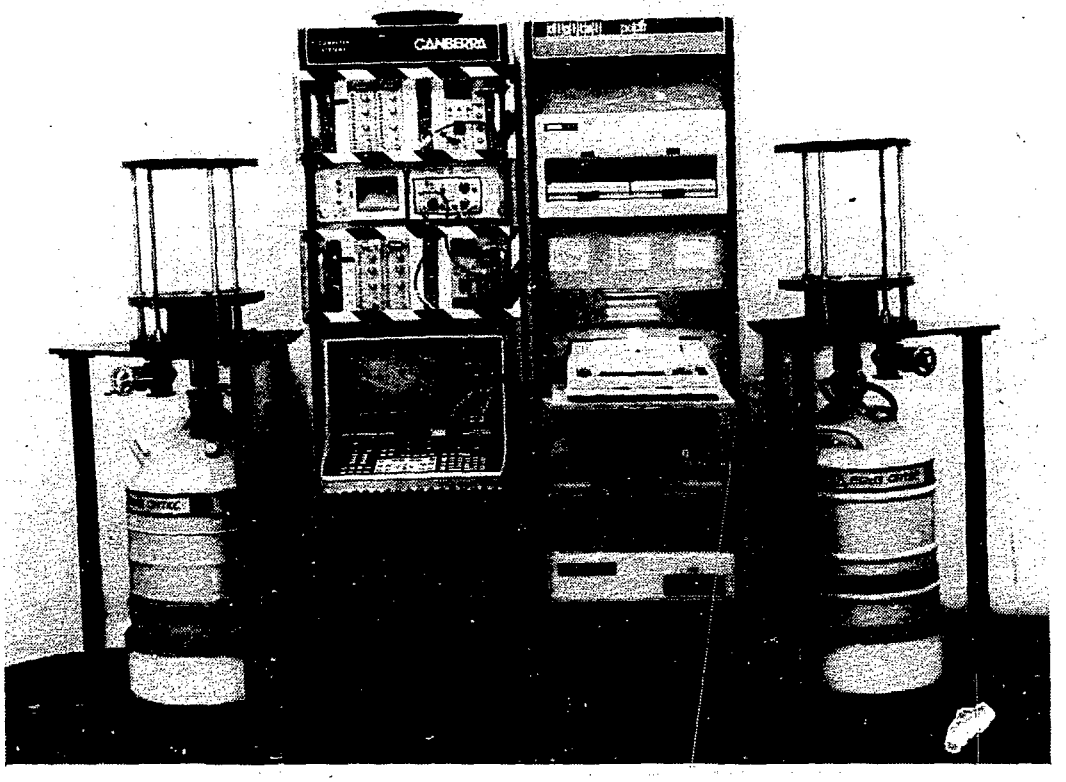

Fig. 21. Los Alamos multiple-detector plutonium isotopic system.

Long-term tailing is not used. The slope of the short-term tail is fixed during initial detector characterization. For each group fit, the peak height and FWHM are freed, and in some cases the short-term tail amplitude is also freed. Over 50 peaks are fit in each spectrum in the region from 120 to 450 keV.

Because this method analyzes more peaks than do simple ROI methods, more isotopic ratio pairs can be formed. However, about the same ones as outlined in Table XV are used for the final ratios. Table XVI tabulates the ratios used in GRPAUT.

By using weighted least-squares techniques, investigators can fit relative efficiency curves to points from ^{239}Pu, ^{241}Pu-^{237}U, and ^{241}Am. Normalization constants are used for the ^{241}Pu-^{237}U and ^{241}Am lines. The functional form of the relative efficiency curve is

$$\ln \varepsilon_i = A_o + \sum_{j=1}^{2} A_j / E_i^j + \sum_{j=1}^{3} A_{j+2} (\ln E_i)^j + A_6 \delta_6 + A_7 \delta_7 \quad ,$$

TABLE XVI

PEAK RATIOS CALCULATED IN GRPAUT

Ratio	Energies
241/239	208/203 keV[a]
	148/144 keV
	165/161 keV
	148/129 keV[a]
238/239	153/144 keV
238/241	153/148 keV[a]
240/239	160/161 keV
240/241	160/165 keV
	160/148 keV[a]
Am/239	125/129 keV
	335/345 keV[a]
	369/375 keV[a]

[a]Denotes ratios used to calculate isotopic fractions. Weighted averages used where appropriate.

where ϵ_i is the relative efficiency for a gamma ray of energy E_i. The A_6 and A_7 terms normalize the ^{241}Pu-^{237}U and ^{241}Am points to the ^{239}Pu points.

An isotopic correlation of the form of Eq. (13) $242 = K \times 240^3/239^2$ is used to predict ^{242}Pu.

Several studies have been published using the data analysis techniques of GRPAUT. A two-detector method[19] uses a planar detector in the 120- to 300-keV region and a coaxial detector in the 300- to 700-keV region. The coaxial detector is heavily filtered to remove counts from photons below 200 keV. This procedure improves the ^{240}Pu and ^{241}Am measurement precision using the 642.48-keV ^{240}Pu and 662.42-keV ^{24}Am gamma rays. Quotable precision

results[19] were similar for the 600- and 160-keV regions with ~2% precision for the 160/148 $^{240}Pu/^{241}Pu$ ratio and the 642/646 $^{240}Pu/^{239}Pu$ ratio in a 50-ks counting time. For ^{241}Am the 662/646 $^{241}Am/^{239}Pu$ ratio was significantly more precise than the 125/129 $^{241}Am/^{239}Pu$ ratio for large samples.

Simultaneous calorimeter/gamma-ray assay[33,34] (Fig. 22) has the advantages of reducing operator radiation exposure through less sample handling and of reducing data transcription errors. Table XVII shows the results from simultaneous assay at three sites using a transportable system. These samples ranged from a few hundred grams to 2 kg of oxide and metal, most nominally 6% ^{240}Pu. Count times were generally 10 to 50 ks.

This technique shows overall accuracy of better than 1% with measurement precision for total plutonium in the 1% to 3% RSD range.

The GRPAUT program has also been applied to the case of heterogeneous distribution of americium and plutonium as discussed previously.[23]

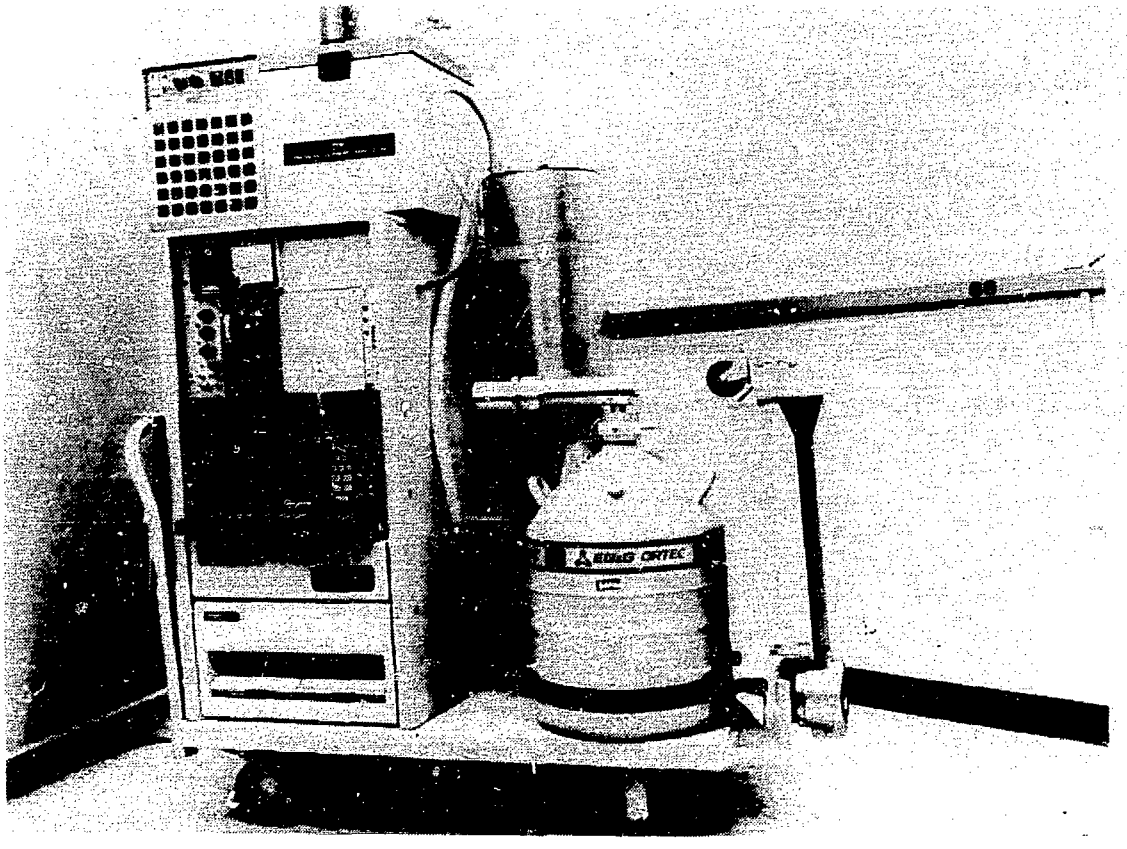

Fig. 22. Transportable calorimetry with simultaneous calorimetry/gamma-ray spectroscopy capability. (Photo courtesy of J. G. Fleissner, Mound Facility.)

TABLE XVII

SIMULTANEOUS ASSAY WITH TRANSPORTABLE CALORIMETER/ GAMMA-RAY SPECTROSCOPY SYSTEM[34]

Site	No. of Samples	Total Pu Assay Average Ratio Measured/Accepted	Rel. Std. Dev. of Individual Ratio
1	18	0.997	1.7%
2	20	1.007	0.7%
3	13	1.00	3.0%

D. Livermore

The response-function form of analysis has seen extensive use by Gunnink and coworkers at Livermore. One of the first implementations of this method was installed at the Savannah River Plant in the early 1970s to measure low-concentration solutions of low-burnup plutonium. Use of the 100-keV region and 40-keV region for fresh samples enables one to obtain significantly better precision than methods using gamma rays above 120 keV. Table XVIII tabulates some results for this system.

For the freshly separated samples, measurement precision in only 10 min is within about a factor of 2 of that customarily assigned to mass spectrometry. The Savannah River system uses 10 mℓ of solution in a plastic vial placed on top of the detector. The solution depth (~1 cm) and low concentration combine to produce small attenuation corrections for these samples.

This technique was applied later to reprocessing-plant solutions of high burnup (~20% ^{240}Pu) and high concentration (~250 g Pu/ℓ).[11] In this situation the 40-keV region is used for fresh solutions, as are the 129-keV ^{239}Pu and 148-keV ^{241}Pu peaks and the 94-keV UKα_2 x ray. Simple ROI integration is used for peak areas, with interferences stripped out channel by channel before summing. Absolute concentration for each isotope is measured with the system being calibrated with known solutions. The plutonium isotopic fractions are computed as outlined in Sec. IV.B. For aged solutions, response-function methods are applied to the 100-keV region. The 208- and 59-keV peaks are used for energy calibration and adjustment of peak-shape parameters. Numerous interferences are stripped out of the 100-keV complex before the response function fits are made.

TABLE XVIII

FRESHLY SEPARATED SAMPLES
10-min MEASUREMENT, 3 g Pu/ℓ SOLUTION[4]

Isotope	Abundance (%)	Av Bias (%)	Precision (% RSD)
238	0.008	5.6	4.7
239	93.46	0.048	0.049
240	5.88	0.75	0.72
241	0.65	0.96	1.9

AGED SAMPLES
60-min MEASUREMENT, 5.4 g Pu/ℓ SOLUTION[4]

Isotope	Abundance (%)	Av Bias (%)	Precision (% RSD)
238	0.018	7.6	5.7
239	90.92	0.14	0.09
240	8.40	1.6	0.94
241	0.661	0.64	0.61
Am	-	0.08	0.26
Total Pu	5.4 g/ℓ	0.46	0.35

A very thin (~1 mm thick) sample cell, shown in Fig. 23, allows about a 0.25-mℓ sample to be viewed. The cell is mounted on the detector face as shown in Fig. 24.

Fresh solutions are counted for 15 to 30 min; aged solutions are counted for 30 min to 1 h. An isotopic correlation of the form of Eq. (12) is used to predict ^{242}Pu.

Summarizing the large amount of data on process solutions taken with this system is difficult. Table XIX attempts to list the extremes for isotopic abundance, bias, and precision for both aged and fresh solutions.

Ruhter and Camp[30] have also applied response-function techniques to solid samples using gamma rays in the 120- to 450-keV region. This analysis package is made portable for use by International Atomic Energy Agency inspectors.

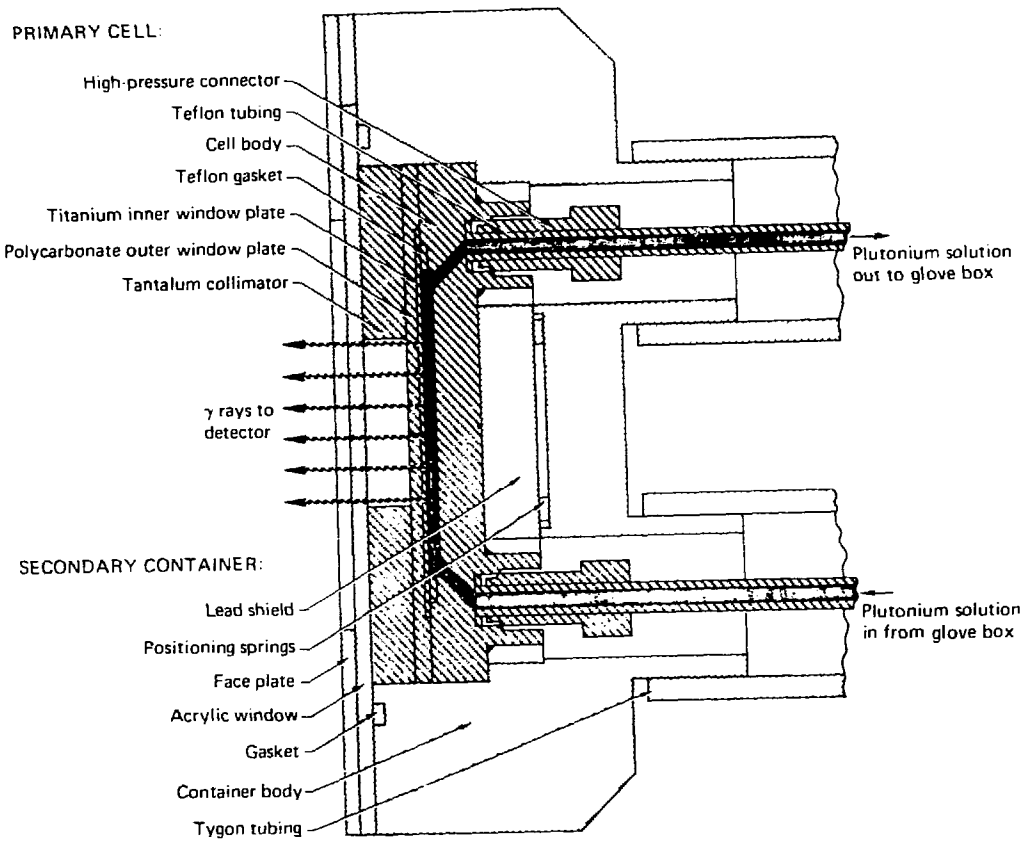

Fig. 23. Cutaway view of sample cell and double containment.[11] (Photo courtesy of R. Gunnink, Lawrence Livermore National Laboratory.)

TABLE XIX

REPROCESSING PLANT SOLUTIONS, 130-270 g Pu/ℓ, 94 SAMPLES
TASTEX TASK H PLUTONIUM ISOTOPICS[11]

Isotope	Abundance Range (%)	Abs. Value Bias Range (%)	Abs. Value Precision Range (% RSD)
238	0.5 - 1.0	0.1 - 0.8	0.4 - 0.7
239	60 - 75	0.01 - 0.3	0.08 - 0.4
240	17 - 23	0.02 - 0.4	0.2 - 1.3
241	5 - 11	0.02 - 0.8	0.2 - 0.8

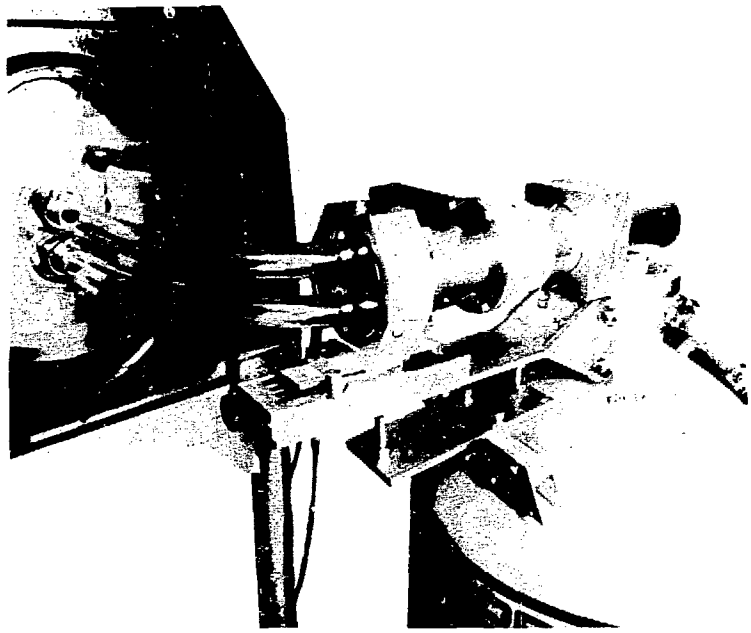

Fig. 24. Sample-cell assembly mounted on detector and coupled to glove box.[11] (Photo courtesy of R. Gunnink, Lawrence Livermore National Laboratory.)

Another system described by Gunnink[35] makes use of all the data available in the spectrum, accommodates two detectors (high and low energy), and analyzes data with both response functions and ROI peak integration. This system can obtain better precision than other methods for arbitrary samples because of its response-function analysis of the 100-keV region.

E. Precision Summary

Measurement precision is influenced most by the spectral region analyzed, with higher precision obtained for the lower energy regions that have higher emission rates. In Table XX we attempt to summarize the measurement precision attainable for different energy regions, with the ranges corresponding to a reasonable range of count times and isotopic abundances. Accuracy is usually commensurate with precision.

TABLE XX

TYPICAL MEASUREMENT PRECISION (% RSD)

Energy Region (KeV)	Count Times	238	239	240	241	Am	Specific Power
40	10-30 min	0.3-5	0.05-0.5	0.2-1.0	0.2-1.0	-	-
100	30-60 min	0.3-5	0.05-0.5	0.2-1.0	0.2-0.8	0.1-1.0	0.1-1.0
>120	1- 4 h	< 1-10	0.1 -0.5	1-5	0.3-0.8	0.2-10	0.3-2

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